Preliminary Evaluation of AFBC Solid Waste Properties, 1982/83

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September 1985

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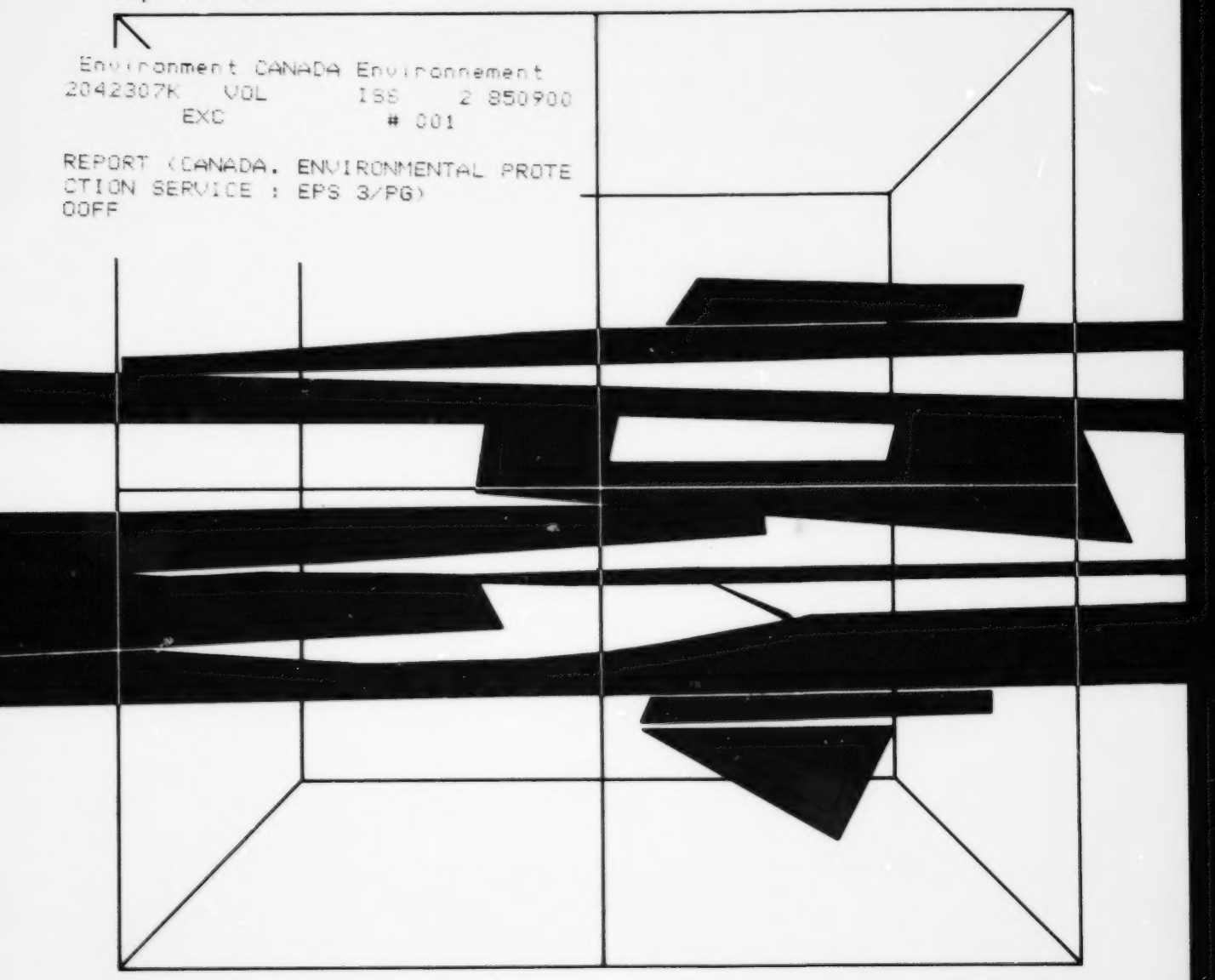

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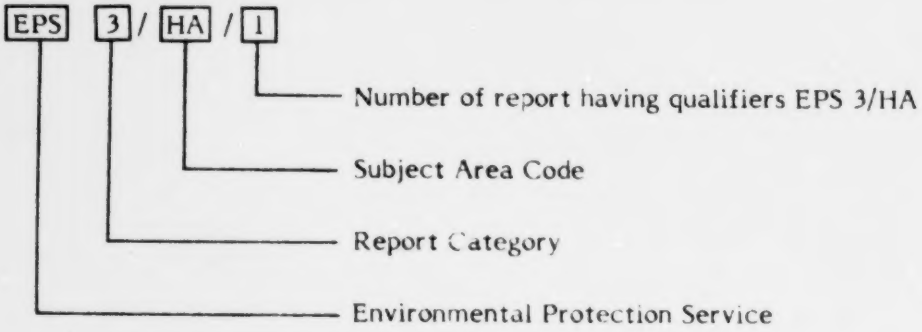

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PRELIMINARY EVALUATION OF AFBC SOLID WASTE PROPERTIES, 1982/83

by
Dearborn Environmental Consulting Services
and the Wastewater Technology Centre
Environmental Protection Service
Environment Canada

for the
Oil, Gas & Energy Division
Industrial Programs Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Environment Canada

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ABSTRACT

Literature reviews and laboratory studies were conducted to provide preliminary information on the properties of atmospheric fluidized bed combustion (AFBC) solid residues and to allow comparisons with conventional pulverized coal-fired (PCF) wastes and PCF flue gas desulphurization wastes. Two AFBC spent bed materials and one baghouse material were subjected to a variety of laboratory tests and analyses to evaluate their physical, chemical, exothermic and leaching properties. The wastes were generated during the combustion of Canadian high-sulphur coal and a mixture of high-sulphur coal and woodchips in a limestone bed at an AFBC test facility.

The residues were highly alkaline and composed primarily of calcium and sulphur salts. Significant quantities of crystalline calcium oxide were found in these residues. This was unusual in comparison to conventional coal combustion residues, and appeared to be the main cause of exothermic reactions between the residues and water. Temperature increases of up to 55°C were recorded at low liquid-to solid ratios and temperatures above 100°C were observed.

Permeability coefficients of the bed residues, at 2.4×10^{-2}, indicated these materials were relatively permeable and comparable to sands in this regard.

Leachates from the bed materials, generated during 10 and 20 cycle serial batch leaching tests, remained at pH 12 throughout the tests when distilled water was the leaching medium. The pH levels only dropped after several leaching cycles with acidic medium. Total dissolved solids concentrations remained relatively high throughout these tests and the primary constituents were calcium and sulphate.

The results of this preliminary study suggest that AFBC wastes have some unique properties in comparison to conventional pulverized coal-fuelled combustion wastes. These results, however, may not be representative of other AFBC residues. Further studies of a greater variety of fresh AFBC residues are now required to verify these findings and to determine if the potential waste management and disposal problems indicated in this study are of general concern for this new waste type.

RÉSUMÉ

Des études bibliographiques et en laboratoire ont été effectuées dans le but de fournir des données préliminaires sur les propriétés des résidus solides de la combustion en lit fluidisé à la pression atmosphérique (CLFPA) et d'établir des comparaisons avec les propriétés des résidus ordinaires obtenus par combustion avec du charbon pulvérisé (CCP) et de ceux résultant de la désulfuration des fumées par CCP. Deux résidus de CLFPA et le contenu d'un dépoussiéreur à sacs filtrants ont été soumis à divers essais et à différentes analyses en laboratoire dans le but de déterminer leurs propriétés physiques, chimiques, exothermiques et lixiviantes. Les résidus ont été obtenus au cours de la combustion, dans une installation pour les essais de CLFPA, de charbon canadien à forte teneur en soufre et d'un mélange de copeaux de bois et de charbon du même type en lit de calcaire.

Les résidus étaient très alcalins et comprenaient surtout des sels de calcium et de soufre ainsi qu'une bonne quantité d'oxyde de calcium cristallisé. Comparativement aux résidus de la combustion classique au charbon, cette composition est exceptionnelle et semble être la principale cause des réactions exothermiques entre l'eau et les résidus. Des augmentations de température allant jusqu'à 55°C ont été enregistrées à de faibles rapports liquide-solide.

Le pH du lixiviat des résidus est demeuré à 12 lorsque de l'eau distillée a été employée pour 10 et 20 cycles de lixiviation en discontinu, et il n'a diminué qu'après plusieurs séries de lavages en milieu acide. Au cours de ces essais, les concentrations de solides totaux dissous, comprenant surtout du calcium et du sulfate, sont demeurées relativement élevées.

Les résultats de cette étude préliminaire indiquent que les résidus de la CLFPA, comparativement à ceux de la CCP classique, possèdent certaines propriétés uniques; il est cependant possible qu'ils ne soient pas applicables à d'autres résidus de la CLFPA. Il est maintenant nécessaire d'effectuer d'autres études portant sur une plus grande variété de résidus fraîchement obtenus par CLFPA pour confirmer ces résultats et savoir si les problèmes éventuels de gestion et d'élimination des déchets qui apparaissent à la lumière de cette étude sont généralisés pour ce nouveau type de résidu.

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1 BACKGROUND AND STUDY OBJECTIVES

1.1 Background

Atmospheric fluidized bed combustion (AFBC) is being developed as a combustion technology for the production of energy from low and variable quality solid fuels, and as a simple alternative means to control sulphur emissions from high sulphur content coals. For sulphur emission control, coarsely crushed coal is burned in a bed of limestone that has been fluidized by jets of heated air (Figure 1). The sulphur in the coal reacts with the calcium oxide formed in the limestone bed. Generally, combustion occurs at around 850°C which is considerably lower than the temperatures normally encountered in conventional coal-fuelled boiler systems. The lower temperature results in decreased nitrogen oxides formation and emission. Other advantages of AFBC systems include reduction of the physical size of the boiler due to improved heat transfer efficiency, and the ability to burn low quality fuels without the slagging or fouling problems normally encountered in conventional pulverized coal-fired (PCF) boilers (Mayfield, 1981).

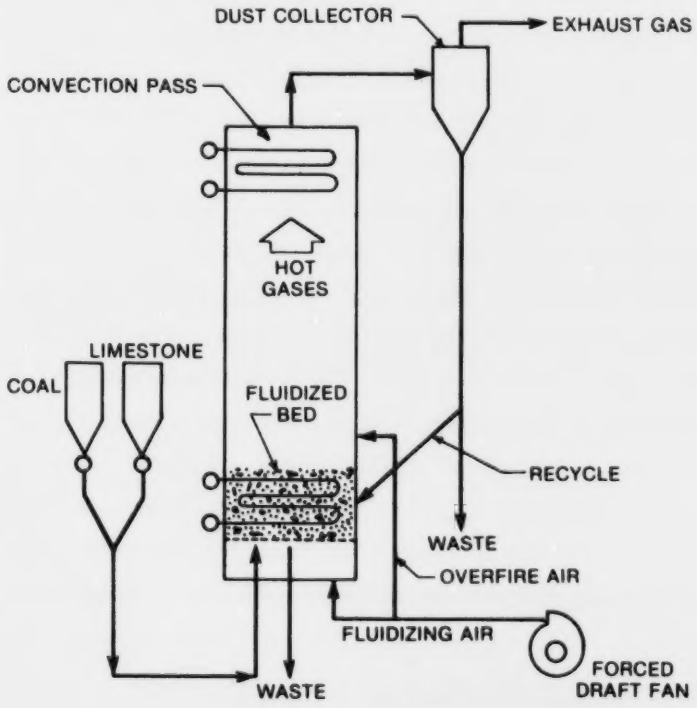


FIGURE 1 SIMPLIFIED AFBC SCHEMATIC

The major emphasis in AFBC development to date has been on improving the combustion design and on reliable operation. There has also been a growing awareness of problems and the potential environmental consequences of waste generation, handling, and disposal. Instead of the usual bottom ash, fly ash and flue gas desulphurization (FGD) sludge residues which are normally produced from FGD equipped pulverized coal-fired units, the AFBC process generates a dry spent bed material and "fly ash" or elutriated bed material, which both contain the captured sulphur. The weight of solid wastes from AFBC units burning high sulphur coal in limestone, can be several times that produced by conventional PCF units without flue gas scrubbers (EPS, 1982). With high sulphur coal and stringent sulphur removal requirements, present AFBC designs may even produce greater volumes of waste than FGD equipped systems.

The environmental implications of solid wastes generated by AFBC units are not well documented. In previous studies it was found that available information on physical and chemical characteristics of AFBC wastes was incomplete and sometimes contradictory (e.g., CH2M Hill, 1982).

1.2 Study Objectives

Major objectives of this study included the development of preliminary information on the physical, chemical and leaching properties of AFBC wastes in order to permit comparisons with conventional PCF and PCF/FGD wastes. This information was also required to assess the need for the development of AFBC waste testing protocols and specific recommendations for safe waste handling and disposal.

For these purposes, further reviews of the technical literature to document the known properties of AFBC wastes and extensive laboratory tests to examine the physical, chemical, exothermic and leaching properties of AFBC waste samples were conducted. These studies were undertaken in several phases. The initial phases consisted of preliminary literature reviews, preliminary evaluations of some of the properties of three AFBC waste samples and preliminary tests of methods that might be used to measure these properties. The following phases consisted of detailed technical literature searches and evaluation as well as detailed tests and analyses to characterize three AFBC residues. Summaries of the results of the early phases are incorporated in this report with the final detailed laboratory studies.

2 LITERATURE REVIEW

2.1 Introduction

The general physical and chemical properties of AFBC solid wastes have been, to some degree, characterized in a number of research studies conducted by government agencies and private corporations in North America and Europe. It is very difficult to generalize from these studies or to extrapolate with much confidence to the anticipated Canadian situation because a wide variety of fuels, bed materials, characterization methods and AFBC designs have been employed. Consequently, different study results often appear to be contradictory. The magnitude of the problem becomes apparent when the large number of factors that may influence the various properties of AFBC solid wastes are considered. The factors considered by Sun et al. (1978) to be the most important include:

1) Coal properties, such as sulphur content, heating value and ash content.
2) Fresh sorbent properties, such as type of sorbent (limestone or dolomite), composition, physical structure and attrition behaviour.
3) Fluid bed combustion system concepts, such as power cycle, once through or regenerative operation and sorbent pretreatment.
4) Fluid bed combuster designs and operating conditions, such as temperature, pressure, excess air, residence times of sorbent and gas, calcium-to-sulphur feed ratio, superficial velocity, coal and sorbent feed sizes and rates, internal design, distributor design and turndown operating conditions.
5) Regeneration process concepts, such as one-step (high temperature) or two-step (low temperature) processes, point of fresh sorbent feeding and point of spent sorbent withdrawal.
6) Regenerator design and operating conditions, such as temperature, pressure, reactant gas (or solid reductant) composition, residence times of sorbent and gas, multiple stages or regions, internals design, distributor design and superficial velocity.
7) Design of other system components, such as particulate control and sorbent circulation.

The technical literature contained only scattered information on the properties of AFBC solid wastes of potential environmental protection significance. Consequently emphasis in this review was placed on summarizing this limited information and

identification of the most promising methods that other researchers have used to quantify these properties.

2.2 Physical Properties of AFBC Solid Wastes

The physical properties of AFBC solid wastes that appear to be important from an environmental viewpoint (i.e., for handling and disposal considerations) are: moisture content, specific gravity, density, moisture-density compaction relationships, water holding capacity, permeability and particle size distribution. Stone and Kahle (1978) presented information on some of these physical properties for a spent bed material and fly ash from an AFBC unit. The specific gravities of the bed and fly ash materials were 2.8 and 2.65 g/cm^3, respectively. The dry density of the fly ash was 0.76 g/cm^3 both before and after slaking. The bed material density increased slightly from 0.92 to 0.97 g/cm^3 after slaking. This relative stability, however, does not appear to be consistent with other reports. Pope et al. (cited in Stone and Kahle, 1978) indicated that the dry density of one spent bed material they tested decreased by 49% after slaking, whereas another increased by 48%. The water holding capacity (i.e., the amount of water that can be retained against the force of gravity) was 66% for the fly ash and ranged between 44% and 98% for the spent bed material. The permeability coefficient of the bed material ranged between 6.8×10^{-4} and 3.7×10^{-2} cm/s. The permeability coefficient of the fly ash was 1.9×10^{-3} cm/s. This compares favorably with the range of permeability coefficients of 1.0×10^{-3} to 5.0×10^{-2} cm/s reported by Integ (1979) for a compacted fly ash from a different AFBC unit. These coefficients are comparable to that of clean fine sand. For additional comparison, the permeability coefficients of gravels can be greater than 11.6 cm/s and those of clays in the order of 1×10^{-7} cm/s. Integ (1979) suggested that permeability coefficients determined using short-term laboratory tests may not be indicative of long-term field disposal situations because of changes in the disposed ash. They stated that some reduction in water permeability, possibly up to 50%, may occur in the ash one or two weeks after disposal.

Integ (1979) also provided results of dry density/moisture content testing conducted on an AFBC spent bed material generated from a British coal and limestone. Density/moisture relationships were established for material compacted into 102 mm cubes using a vibrating hammer. After curing in molds for seven days, the unconfined compressive strength/time relationships for the formed cubes were established using a concrete testing machine. From an initial density of 1300 kg/m^3 in the dry condition, the ash showed a considerable reduction in dry density when small amounts of water were

used in the formation of the compacted cubes. As the moisture content was increased, a maximum density was achieved followed by a gradual reduction in density (Figure 2). A maximum density of about 1450 kg/m^3 was achieved with a moisture content of approximately 30%. The compressive strengths of the tested AFBC spent bed materials increased linearly with the logarithm of time. Maximum compressive strengths were achieved after 140 days and were approximately 13.8 N/mm^2 (13 789 kPa). Maximum 7 and 28 day strengths were about 1 N/mm^2 (965 kPa) and 8.9 N/mm^2 (8963 kPa), respectively. The optimum compressive strength after 28 days was achieved at a moisture content of 36%, which is approximately the same as that required for a maximum dry density.

Particle size analyses of spent bed material and carryover/fly ash from several AFBC units have been reported (Stone and Kahle, 1978; Integ, 1979; Collins, 1980). Figure 3 shows the results of particle sizing on slaked and unslaked bed material and fly ash using ASTM D422 which requires the use of a hydrometer (Stone and Kahle, 1978). The particle size distributions of the spent bed material shown in Figure 3a were similar to that of sand; however, the slaked bed material distribution was different from that of the unslaked. Minnick (cited in Integ, 1979) suggested that this was due to the relatively high calcium oxide (CaO) content of the material and the particle size reduction which accompanies the slaking reaction. On the other hand, there were no significant differences between the particle size distributions of the slaked and unslaked fly ash. This may have been due to the considerably smaller CaO content in the fly ash compared to the spent bed material. Samples of AFBC carryover/fly ash from the Combustion Power Company showed that two-thirds of the material collected from a secondary cyclone were sized below 0.075 mm (Crowe and Seale, 1978). Since particles trapped in a secondary cyclone are relatively finer than those caught in a primary cyclone, this material contained a significantly higher percentage of fines than the material shown in Figure 3(b) which was comprised of the total carryover stream. The particle size distributions of spent bed materials and fly ashes reported by Integ (1979) and Collins (1980) are shown in Figures 4 and 5, respectively.

2.3 Chemical Properties of AFBC Solid Wastes

The chemical compositions of AFBC wastes should be strongly influenced by the composition of the coal and limestone utilized and to a lesser extent, by the operating conditions in the AFBC unit. While some information exists in the technical literature on the chemical composition of AFBC residues from various units, it is very difficult to

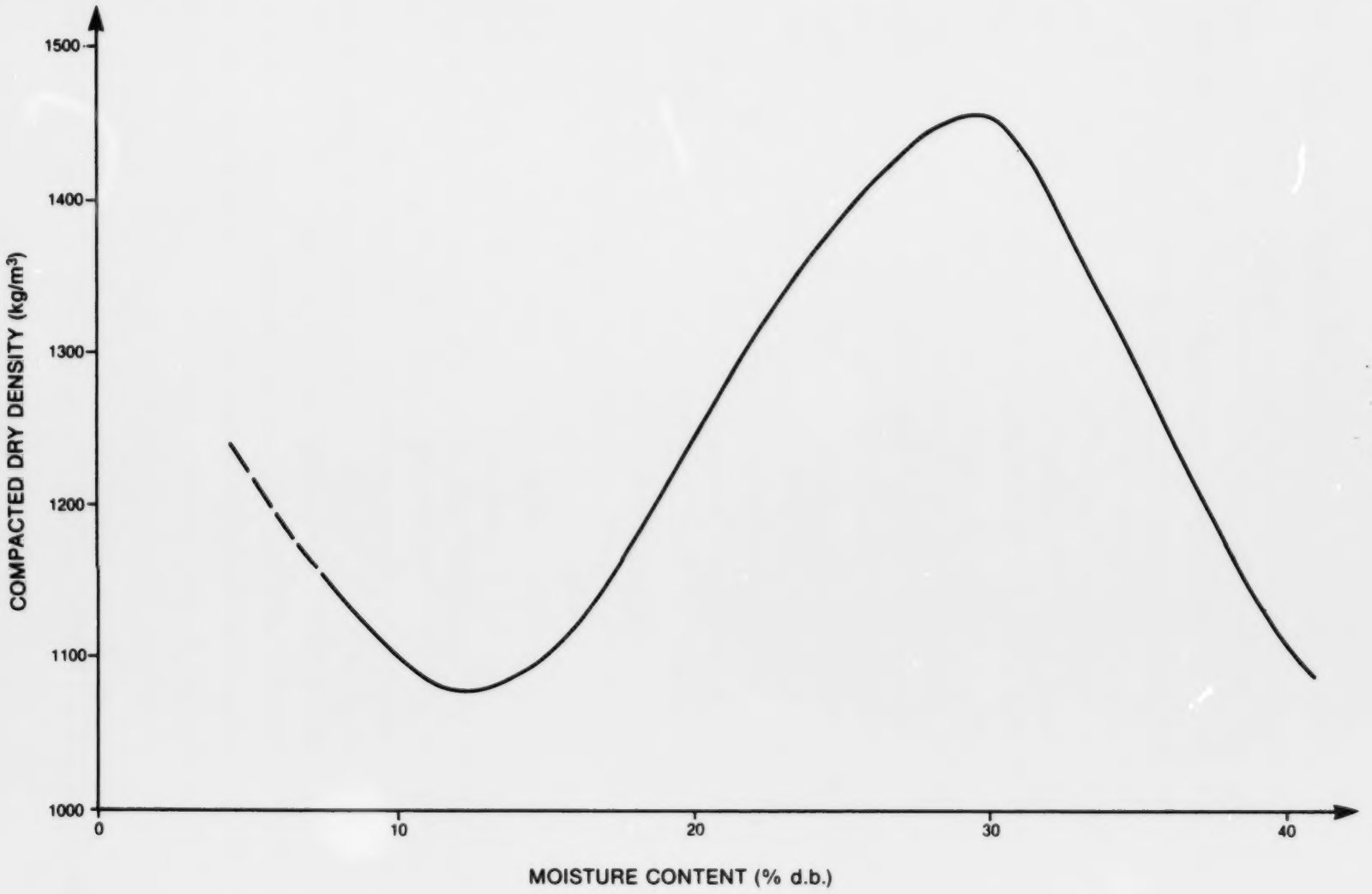
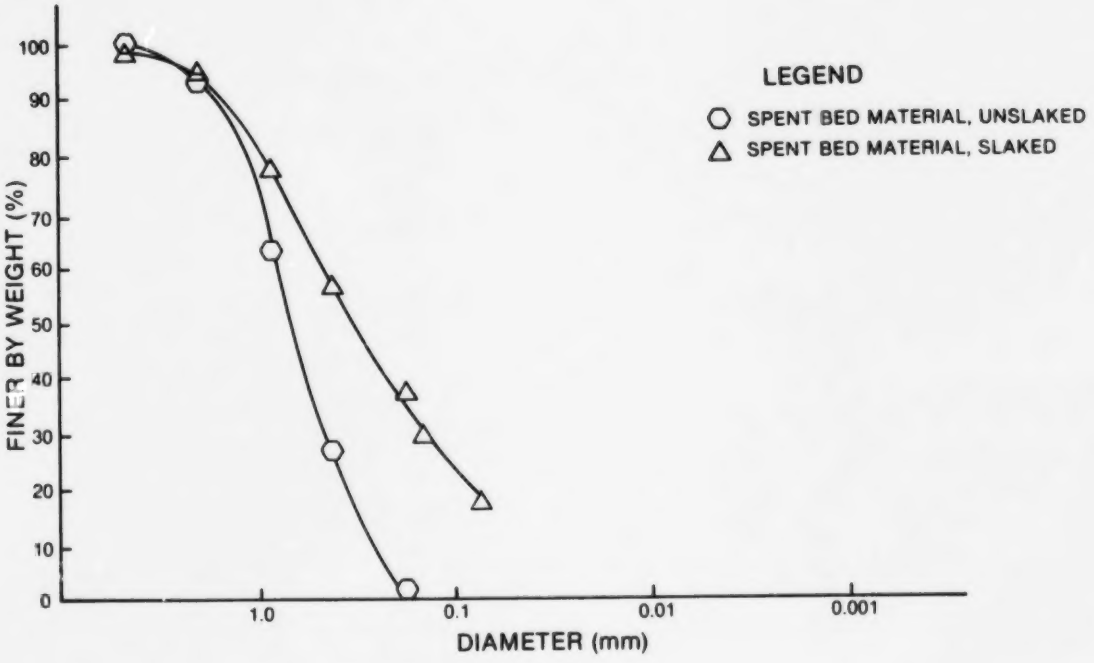
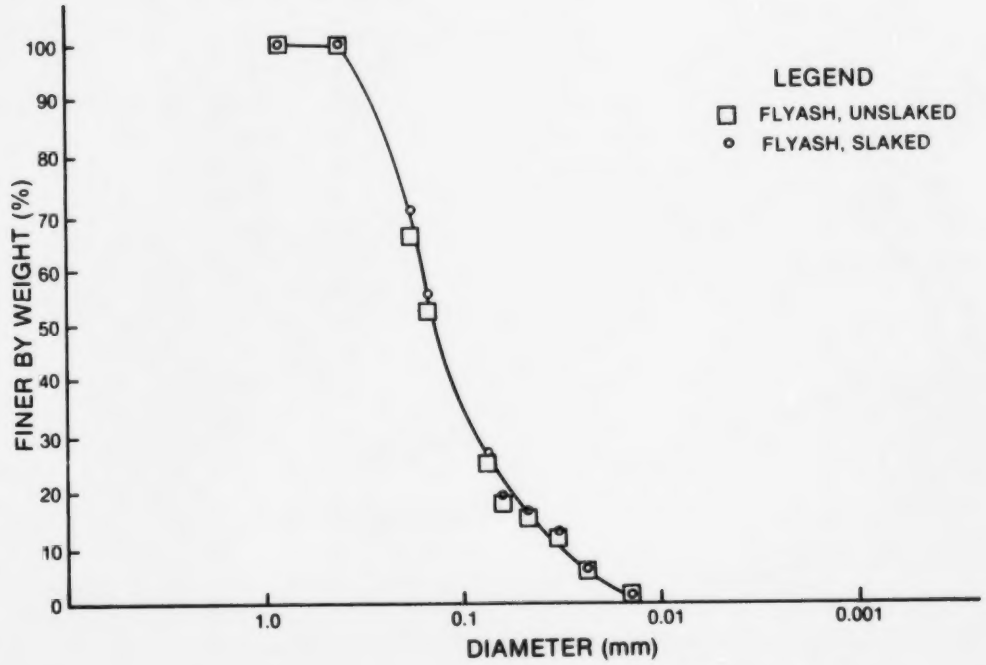


FIGURE 2 MOISTURE CONTENT/DRY DENSITY RELATIONSHIP FROM AN AFBC BED WASTE (Integ, 1979)



a.



b.

FIGURE 3 PARTICLE SIZE ANALYSIS OF SLAKED AND UNSLAKED FBC RESIDUES, ASTM D422 (Hydrometer) METHOD (Stone and Kahle, 1978)

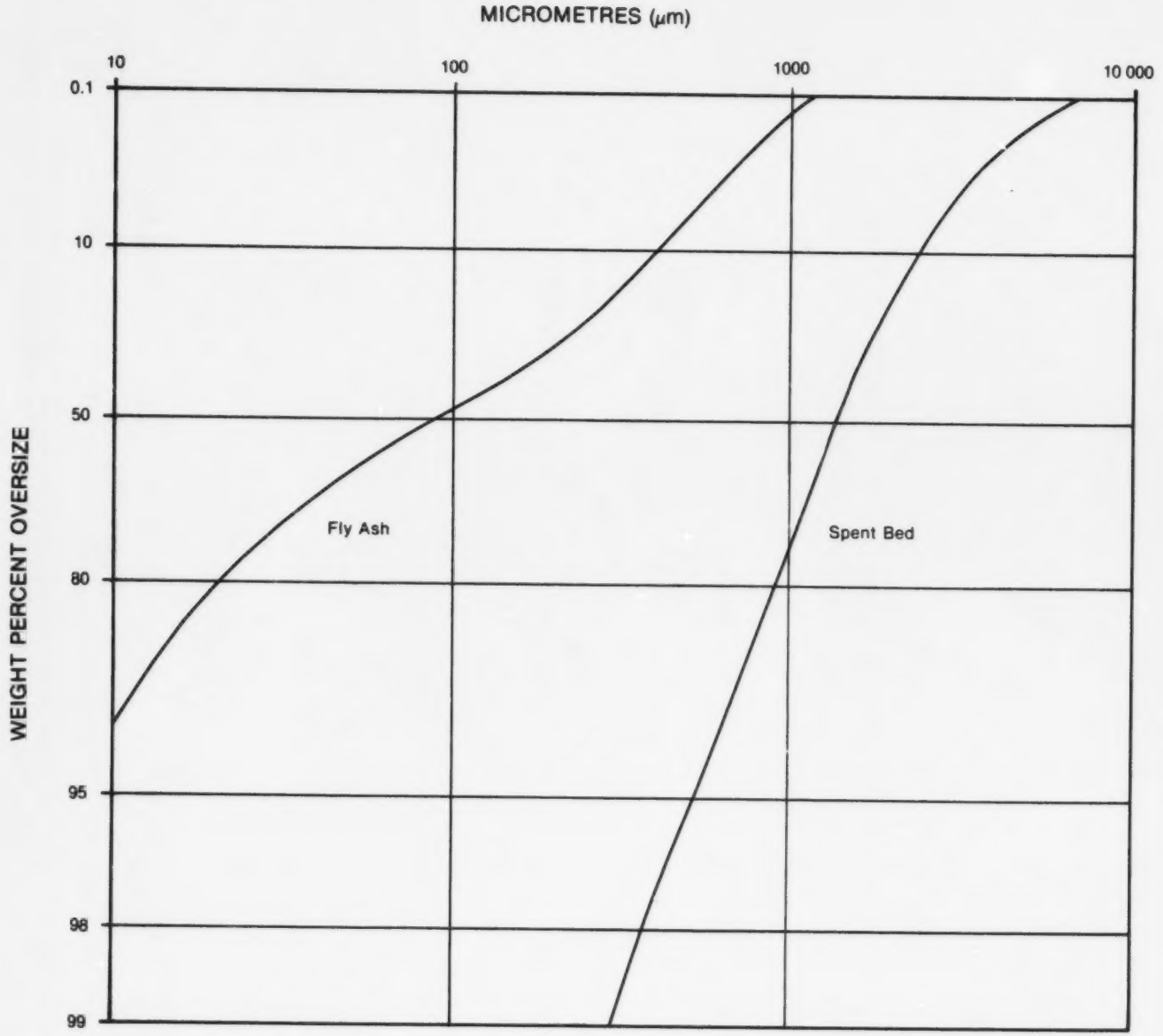
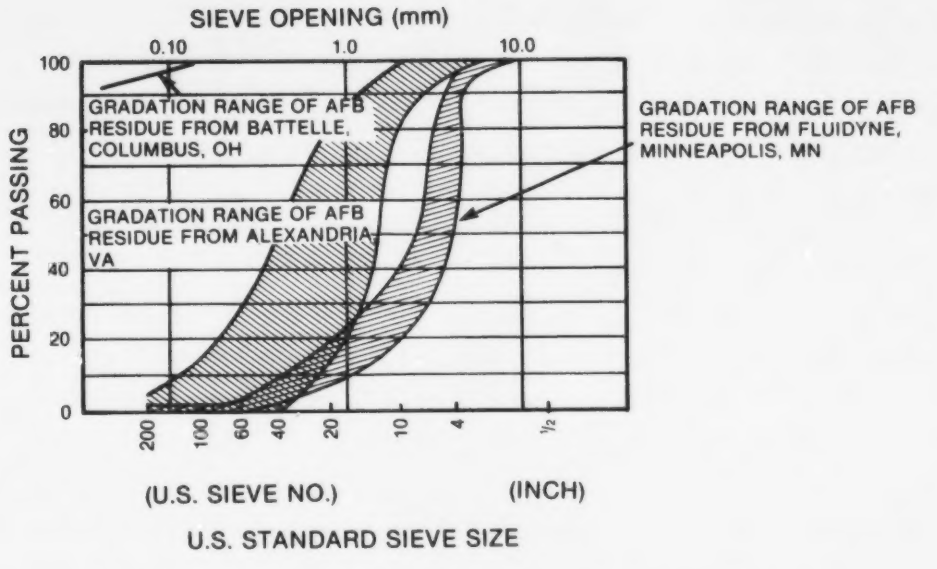
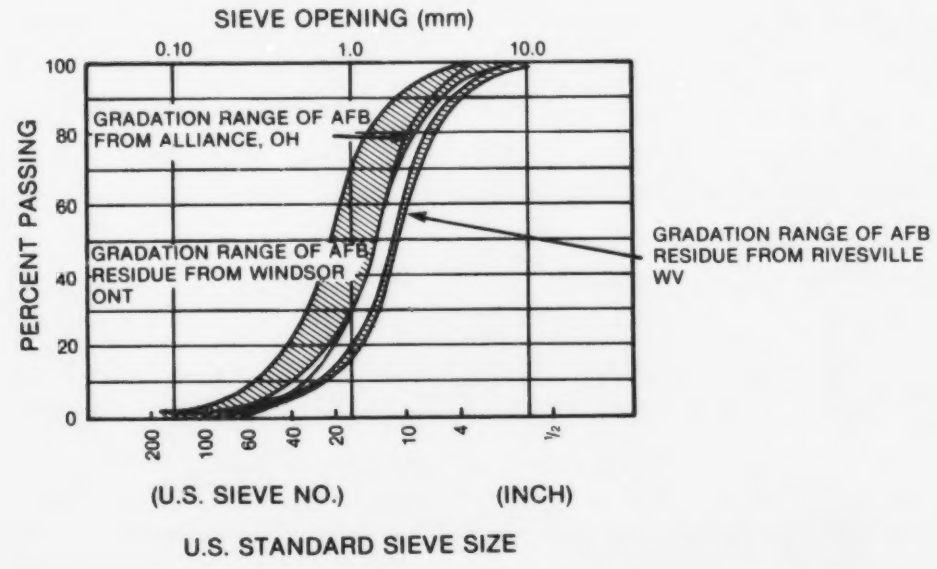


FIGURE 4 TYPICAL AFBC PARTICLE SIZE DISTRIBUTION (Integ, 1979)



GRADATION RANGE OF AFB RESIDUE SAMPLES FROM ALEXANDRIA, FLUIDYNE, AND BATTELLE BOILERS



GRADATION RANGE OF AFB RESIDUE SAMPLES FROM RIVESVILLE, AND WINDSOR BOILERS

FIGURE 5 PARTICLE SIZES OF FIVE AFBC RESIDUES (Collins, 1980)

compare this data with, or project it to, other units if the original fuel and bed compositions as well as the conditions under which the wastes were generated are not provided. Information in this section, therefore, provides only a very general outline of chemical compositions of some AFBC solid residues.

2.3.1 Chemical Composition.

Spent Bed Material

The chemical compositions of spent bed materials from several AFBC sites are shown in Tables 1 and 2. The spent bed material from some AFBC units has been described by Sun et al. (1978) as a coarse, sand-sized, dry solid which contains substantial quantities of calcium sulphate ($CaSO_4$), unreacted calcium oxide (CaO) and trace elements.

The major and minor crystalline compounds in bed materials from five AFBC sites as indicated by X-ray diffraction analyses, are shown in Table 3 (Collins, 1980). The major compounds were calcium sulphate, calcium oxide, silicon dioxide and calcium carbonate; however, there were substantial differences in the composition of the residue from Site No. 2 and the residues from the other sites. In particular, Site No. 2 material contained major quantities of calcium carbonate ($CaCO_3$) but no calcium oxide. This residue was obtained from a boiler using dolomite as the sulphur sorbent, whereas the other residues, each of which contained calcium oxide as a major component, were produced in limestone beds. Collins suggested that the magnesium oxide (MgO) component of dolomite is involved in the sorbent reaction, but not the calcium in carbonate form. The significance of such compositional variations on residue properties, however, still requires further investigation.

The chemical composition of different particle size fractions of spent bed material was investigated by Crowe and Seale (1978). Typical data from two AFBC wastes are shown in Table 4. Although there are no consistent relationships, it appears that the elemental components of some bed material size fractions may be related to particle size.

Studies of the microstructure of waste particles from AFBC units are not widely available yet. The particle structure of solid wastes from a pressurized fluid bed combustor (PFBC) was described by Crowe and Seale (1978). The granular bed material generally consisted of three zones. The outermost zone, or surface layer, ranged in thickness from 2 to 25 μm, and consisted mainly of calcium sulphate. Metal oxides were also present and ranged from low iron oxide concentrations to heavy encrustations of

TABLE 1 MAJOR CHEMICAL CONTENTS OF AFBC BED WASTES FROM SIX UNITS (Sun et al., 1978)

Site	Loss on Ignition*	Silicon	Iron	Aluminum	Calcium	Magnesium	Sulphur
1**	5.79	6.07	2.79	1.23	38.28	1.02	6.66
2***	12.46	7.90	2.71	1.44	20.20	7.17	8.12
3	11.79	6.50	10.10	1.57	29.90	1.92	5.85
4	3.19	6.30	2.88	2.07	34.09	0.58	9.39
5	3.72	1.93	2.67	0.93	40.38	0.12	9.70
6	10.49	1.51	2.84	0.13	40.31	0.65	6.00

Note: all analyses reported in weight percent

* represents carbon and water of hydration
** average of four samples
*** average of two samples

siliceous glass containing large amounts of hematite (Fe_2O_3) and magnetite (Fe_3O_4). The physical integrity of this surface zone ranged from an integral part of the granule body, characterized only by colour and crystal size differences, to a relatively hard and easily separated physical shell which was not well associated with the body of the granule. The second reaction zone, which underlay this surface veneer, ranged from 60 to 150 µm in thickness. In well sulphated samples, this zone extended to the granule's core and consisted of $CaSO_4$ and soft-burned CaO for particles from limestone beds. MgO was sometimes seen in particles from dolomite beds. Granules which were incompletely sulphated had a third zone or core consisting primarily of original material (with the exception of magnesium carbonate ($MgCO_3$) which was not observed) and small amounts of CaO or MgO. The PFBC operating conditions which produced these wastes may have been sufficiently different to produce somewhat different particle structures than those from AFBC units. Nevertheless, these findings may provide some insight into the micro-structure of AFBC solid residues, the reaction mechanisms inside the furnaces and the potential behaviour of the wastes.

Carryover/Fly Ash

The AFBC carryover/fly ash studied by Sun et al. (1978) differed from fly ash from higher temperature combustion units because it was not primarily a siliceous glassy material. The chemical compositions of carryover materials from several AFBC test

TABLE 2 TRACE ELEMENT COMPOSITION OF AN AFBC BED WASTE (Sun et al., 1978)

Analyte	Concentration
Ag	< 0.0001
B	0.005
Be	0.001
Bi	< 0.001
Ca	39
Cd	< 0.003
Co	0.0005
Cr	0.005
Cu	0.003
Mg	> 0.1
Mn	0.019
Mo	0.003
Na	> 0.1
Ni	0.004
Pb	< 0.001
Sb	< 0.0033
Sn	< 0.001
Sr	0.05
Ti	> 0.1
V	0.004
Zn	< 0.0033
SO_4	20

Note: all analyses expressed in weight percent

facilities are presented in Tables 5 and 6. The major chemical elements were reported as common oxide forms by convention. These analyses did not actually provide the oxide or crystalline species contents of these materials. The major chemical elements were silicon, calcium, aluminum, iron, magnesium and sodium. The magnesium and sodium compounds typically occurred in lower concentrations. Quantities of some of these constituents are expected to be dependent upon the compositions of the coal and sorbent

TABLE 3 RESULTS OF X-RAY DIFFRACTION ANALYSES OF FIVE AFBC BED WASTES (Collins, 1980)

	Source of AFBC Residue				
Compound	Site No. 1	Site No. 2	Site No. 3	Site No. 4	Site No. 5
Calcium Sulphate	major	major	major	major	major
Calcium Oxide	major	-	major	major	major
Calcium Carbonate	-	major	minor	trace	trace
Silicon Dioxide	minor	major	minor	major	trace
Mixed Iron Oxides	minor	-	minor	minor	-

In the composition ranges, (-) is 1 percent or less, (trace) is 1 to 5 percent, (minor) is 5 to 25 percent, and major is 25 percent.

used as well as unit operating conditions. For example, the amounts and types of magnesium compounds found will depend on the magnesium in the coal and limestone feedstocks. The amount of $CaSO_4$ in the carryover will depend upon the degree of sulphation and elutriation from the fluidized bed. The amounts of calcium oxide and limestone in the carryover will depend on the degree of calcination, sulphation and elutriation (CH2M Hill, 1982).

2.3.2 Acid Neutralization Capacity. The acid neutralization capacity of a waste is important from an environmental viewpoint because it indicates the potential for a disposed waste to neutralize acidic water contacting the waste, and to condition acidic soils. Stone and Kahle (1978) determined the acid neutralization capacities of spent bed and fly ash materials from two AFBC units burning high sulphur coals. The neutralization capacities, expressed as equivalents of 1.0 N hydrochloric acid per kilogram of material, ranged from 2.6 to 26.0 for the spent bed materials and from 8.8 to 17.5 for the fly ashes. In comparison, pure "slaked lime" or calcium hydroxide ($Ca(OH_2)$) theoretically requires 27.0 equivalents.

2.3.3 Cation Exchange Capacity. Cation exchange capacity is a measure of the total exchangeable cations that a solid can adsorb. The cation exchange capacities of bed and fly ash materials from two AFBC units burning high sulphur coals are shown in Table 7 along with those of several naturally occurring materials for comparison (Stone and Kahle, 1978). The capacities of the bed materials were about 2.0 meq/100 g while those of the fly ashes were 0.5 meq/100 g and 2.4 meq/100 g. These capacities are similar to those

TABLE 4 COMPARISON OF PARTICLE SIZE AND QUALITATIVE X-RAY DIFFRACTION ANALYSIS OF TWO AFBC BED WASTES (Crowe and Seale, 1978)

Sieve Size	$CaSO_4$	CaO	$CaCO_3$	$Ca(OH)_2$	SiO_2	MgO	Fe_2O_3
			Waste No. 1				
+12	major	trace	minor	-	trace	minor	-
-12 to +20	major	minor	minor	-	trace	minor	-
-20 to +30	major	major	minor	-	trace	trace	-
-30 to +60	major	major	minor	trace	-	trace	-
-60 to +100	major	major	trace	trace	-	trace	-
-100 to +200	major	minor	trace	trace	-	trace	-
-200 to +400	major	minor	trace	minor	-	-	trace
-400	major	minor	trace	minor	-	-	-
			Waste No. 2				
+12	major	major	trace	trace	trace	-	-
-12 to +20	major	major	-	trace	trace	-	-
-20 to +30	major	major	-	trace	trace	-	trace
-30 to +60	major	major	-	minor	trace	-	minor
-60 to +100	major	major	trace	minor	-	-	-
-100	major	major	trace	major	trace	-	-

(Major) >30 percent; (Minor) <30 percent, >5 percent; (Trace) <5 percent.

reported for dolomite, limestone, bituminous coal and sand but considerably less than decomposed granite (Table 7).

2.3.4 Organic Matter. Total organic and inorganic carbon concentrations in leachates from processed and unprocessed residues from two pressurized fluidized bed units, and in a control leachate from natural gypsum, were determined by Sun et al. (1978). The measured values were near the analytical detection limit for all leachates, including the control (Table 8). Slightly higher values might be obtained from AFBC wastes.

Concern over the possible presence of toxic organic compounds in AFBC residues stems from the lower combustion temperatures of AFBC units and lower reported efficiencies in some units in comparison to pulverized coal-fired boilers. This lower

TABLE 5 MAJOR CHEMICAL ELEMENT COMPOSITION OF AFBC CARRYOVER WASTES*
(CH2M Hill, 1982) (wt. %)

Coal Type	Source	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	K_2O	S	SO_3	SO_4	P_2O_5	TiO_2
Morgantown Energy Research Centre (sub-butuminous coal)	Cyclone-1	41.7	15.7	20.1	-	3.8	0.6	0.7	1.4	-	-	-	-
	Cyclone-2	40.0	16.8	15.1	-	4.6	1.6	0.8	1.4	-	-	-	-
	Bag Filter	32.9	17.3	24.8	-	6.0	1.4	0.9	2.3	-	-	-	-
Morgantown Energy Research Centre (Texas lignite)	Cyclone -1	Recycled											
	Cyclone-2	44.5	13.3	28.6	6.7	1.3	-	0.6	-	1.9	-	0.5	1.2
	Bag Filter	36.4	14.0	29.6	7.5	2.5	-	0.7	-	4.0	-	0.6	1.2
AFBC Test Facility (bituminous coal)	Fly Ash	17.5	10.5	31.5	12.5	0.4	0.4	1.0	0.4	-	17.0	-	-

* Individual elements are presented in oxide % form only. The elements may actually be present in the wastes in other forms.

TABLE 6 TRACE CHEMICAL ANALYSES OF AFBC CARRYOVER WASTES FROM THREE SITES (Sun et al., 1978)

Analyte	Site No. 1	Site No. 2	Site No. 3	
			Cyclone	Bag Filter
Ag	<0.0001		< 0.0001	< 0.0001
As		0.003		
B	0.02	0.02	0.05	0.05
Be	0.0005	0.001	0.001	0.001
Bi	0.003	< 0.0003	< 0.001	< 0.001
Ca	9.44	16.64	18	16
Cd	<0.0003	< 0.003	< 0.0003	< 0.0003
Co	0.0005	< 0.0005	0.0015	0.0015
Cr	0.005	0.003	0.01	0.01
Cu	0.003	0.005	0.01	0.01
Mg	0.096	2.88	< 0.1	> 0.1
Mn	0.014	0.01	0.011	0.028
Mo	0.001	0.001	0.001	0.001
Na	0.02	0.1	< 0.1	> 0.1
Ni	0.002	0.005	0.007	0.007
Pb	<0.0005	0.001	0.01	0.013
Sb	<0.0033		< 0.0033	< 0.0033
Sn	<0.001	< 0.003	< 0.001	< 0.0001
Sr	0.02		0.1	0.01
Ti	<0.1	0.1	> 0.1	> 0.1
V	0.004	0.001	0.01	0.008
Zn	<0.0033	0.01	0.01	0.01
Zr	1.11	0.01		
S		15.10	4.29	3.96

Note: all analyses reported in weight percent

TABLE 7 CATION EXCHANGE CAPACITIES OF AFBC WASTES AND REFERENCE MATERIALS (Stone and Kahle, 1978)

Material	Cation Exchange Capacity meq/100 g
AFBC Fly Ash*	2.4
Spent Bed Material*	2.4
AFBC Fly Ash+	0.5
Spent Bed Material+	1.9
Limestone	0.6
Dolomite	1.9
Bituminous Coal	2.7
Decomposed Granite	26.6
No. 60 Silica Sand	2.8

Note: * Exxon pilot plant, Linden, NJ
+ Pope, Evans and Robbins, Alexandria, VA

TABLE 8 TOTAL INORGANIC AND ORGANIC CARBON IN LEACHATE FROM UNPROCESSED AND PROCESSED AFBC SOLID WASTE (Sun et al., 1978)

Sample	Residue Leached	Total Carbon (mg/L)	
		Inorganic	Organic
Exxon Bed Material	limestone, pressurized once-through, unprocessed	<7	<5
Exxon Fly Ash	limestone, pressurized once-through, unprocessed	<5	<14
Argonne Bed Material	dolomite, pressurized once-through, unprocessed	<5	<16
Argonne Bed Material	limestone, pressurized once-through, unprocessed	<5	<5
Argonne Regenerator Bed Material	dolomite, pressurized regenerative, unprocessed	<5	<5
Processed Compacts	processed cubes by room temperature blending of Exxon spent sorbent and fly ash	<5	<5
Natural Gypsum	control	<7	<8

combustion efficiency might permit the formation of hazardous organics which might not be completely destroyed at the lower combustion temperatures. However, the combustion efficiency of AFBC units is expected to improve as the technology develops. Results from developmental units do not always reflect the performance of commercial operating units.

In the organic analyses of extracts of FBC materials, no polyaromatic hydrocarbons (PAH), volatile organics or pesticides were detected (Oak Ridge Nat. Lab., 1980). Although small quantities (0.2 ng/L) of polychlorinated biphenyls (PCB) were found, these were thought to have originated from the system blank and not from the waste samples themselves.

In another study, reported by CH2M Hill (1982), unchlorinated dibenzofuran (DBF) was detected in one sample of AFBC residue out of four which were generated under identical operating conditions in the same test facility with different coals. The detection of DBF in only one sample suggests that fuel content may be as important as temperature and operating conditions in contributing to the formation of organic compounds.

2.3.5 Biochemical Oxygen Demand. Stone and Kahle (1978) determined the 5-day biochemical oxygen demands (BOD_5) of AFBC residues in water extracts and distilled water, for comparison (Figure 6). The time lag of one to two days, during which time the BOD was inhibited, indicates that the waste extracts may have contained substances which acted as temporary inhibitors to the growth of microorganisms. Further biological and chemical testing might indicate the nature of this inhibition.

2.4 Exothermic Properties of AFBC Solid Wastes

Atmospheric fluidized bed combustion wastes generated in limestone beds may contain significant amounts of unslaked calcium oxide. The reaction between CaO and water, called slaking or hydration, is exothermic. The heat of hydration of less than half a kilogram of CaO is, theoretically, sufficient to raise the temperature of a litre of water from below freezing to boiling (Boynton, 1966). The heat evolved in the reaction shown below amounts to 1.14 MJ per kilogram of anhydrous CaO.

$$CaO + H_2O \rightarrow Ca(OH)_2 + \text{Heat}$$

When quicklime is exposed to water, it exhibits a strong affinity for moisture. This results in an increase in crystal volume due to the incorporation of water molecules into the lime crystal structure, and release of heat of hydration. This exerts a great

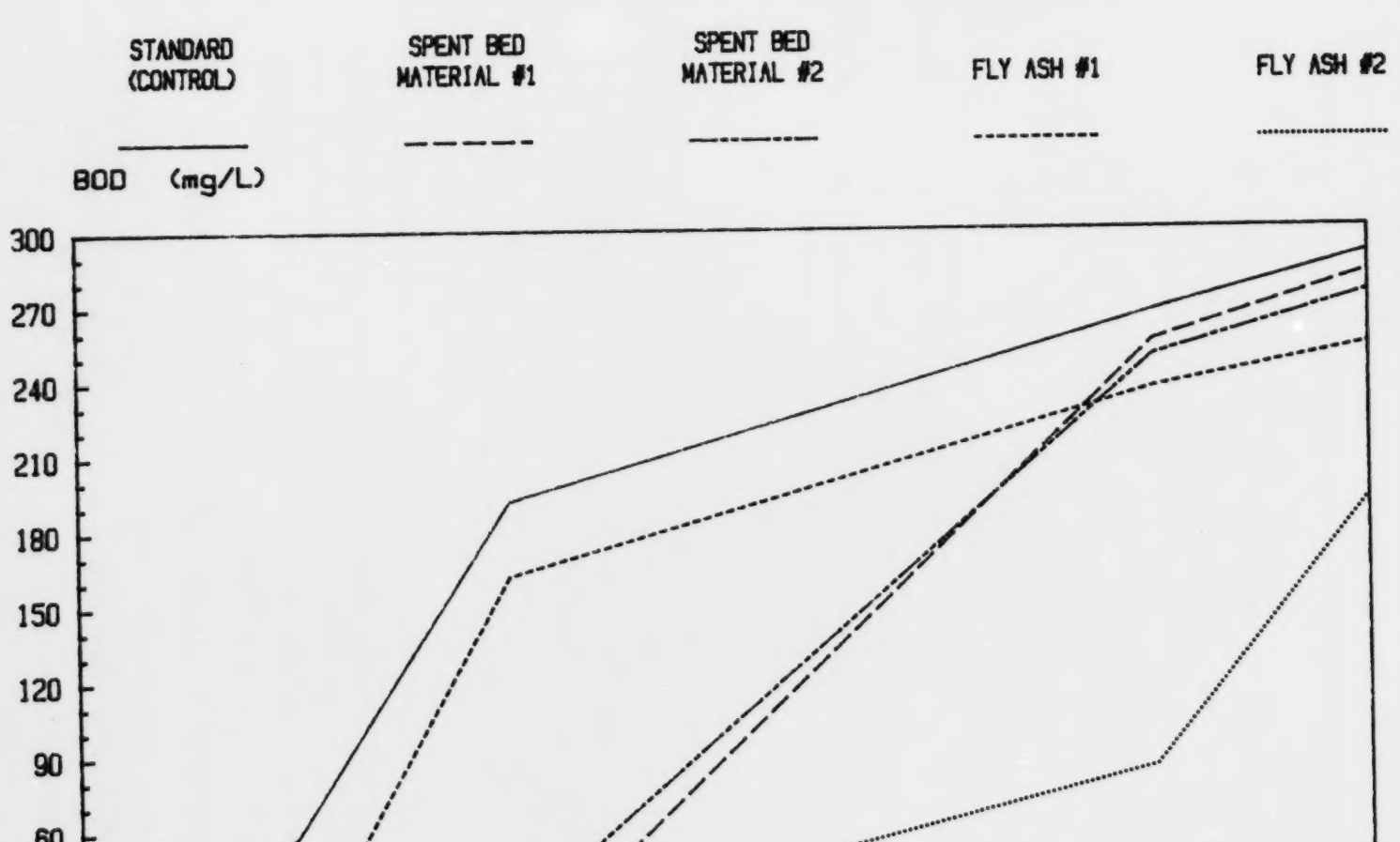


FIGURE 6 FIVE DAY BIOCHEMICAL OXYGEN DEMAND OF AFBC RESIDUE WATER EXTRACTS

internal expansive force in the quicklime particle which causes it to fracture, shatter and then disintegrate completely into microparticles, either as a crystalline dust or as a colloidal suspension. In general, the rate of reaction with water increases with increasing quicklime surface area (Kunesh, 1976). The ratio of water to quicklime determines, in part, the temperature rise.

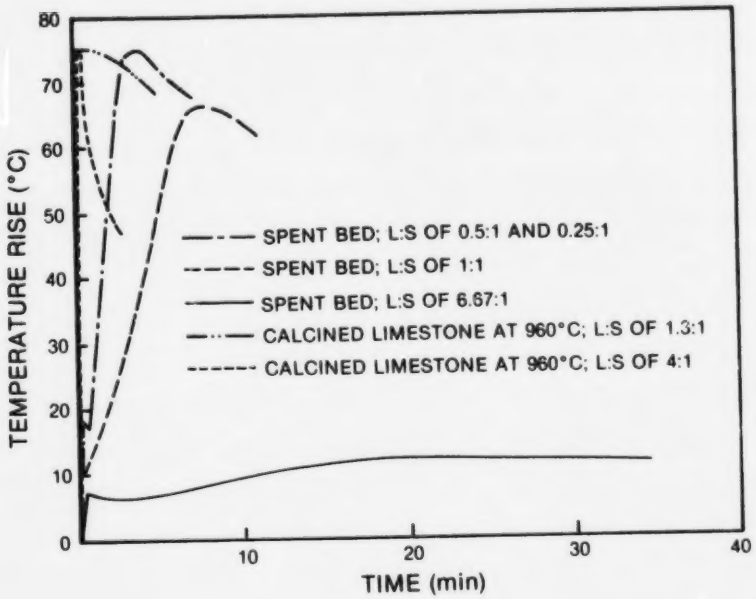
Several researchers have investigated the exothermic properties of AFBC wastes through heat release tests on spent bed and carryover/fly ash materials from several AFBC units (Sun et al., 1978). Temperature rises in an AFBC spent bed material and in calcined limestone at various liquid-to-solid ratios are shown in Figures 7(a) and 7(b). Higher temperature rises and faster responses were observed at lower liquid-to-solid ratios. The maximum temperature rise observed in these spent bed materials at the lowest liquid-to-solid ratio was approximately 75°C.

Stone and Kahle (1978) reported the slaking temperature for a spent bed material reached a maximum of 220°C after 1000 seconds using a liquid to solid ratio of 0.28:1. The fly ash from the same AFBC unit was considerably less exothermic and only increased by 1°C and 13°C. Figure 8 illustrates the temperature versus time relationship for the slaked samples. For a different AFBC unit, fly ash temperature rose to 35°C while the corresponding bed material temperature reached 100°C over the times in Figure 8. Unfortunately, not all studies included information on the form of calcium in the material tested or complete information on the test conditions, such as rate and method of water addition and the elapsed time at which the maximum temperature of the reaction was obtained. Consequently, direct comparisons between results are difficult and may appear contradictory. These differences might be largely accounted for by calcium oxide contents if they were accurately known.

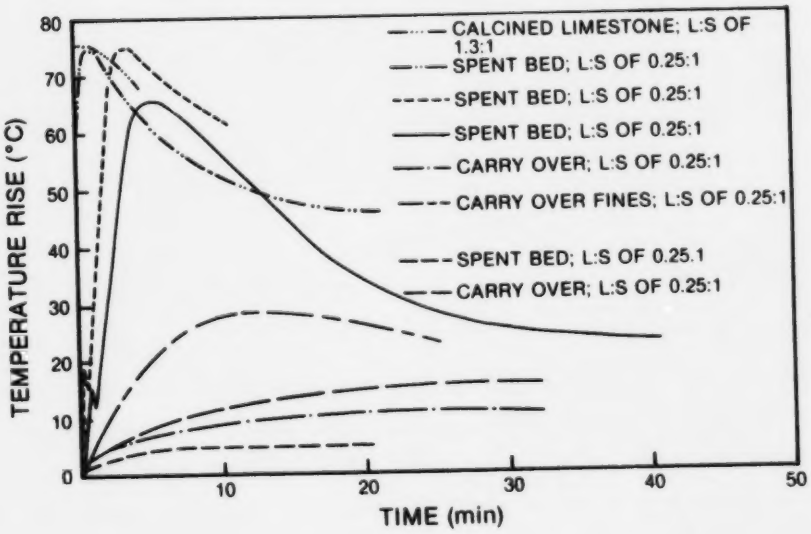
Chemical analyses for elemental calcium in combustion and other wastes are frequently reported, by convention, as the most "probable" or "common" oxide, which is CaO. This convention may be misleading if exothermic properties are of interest because results do not necessarily indicate the amount of calcium present as unreacted, crystalline, calcium oxide (CaO). If this convention is misinterpreted, two substances with apparently similar "CaO" contents may actually have significantly different exothermic properties because of their quite different crystalline CaO contents.

2.5 Leachability of AFBC Solid Wastes

Leachates from several AFBC residues were analyzed for pH, calcium, magnesium, sulphate, trace metal concentrations and total organic carbon by Sun et al.

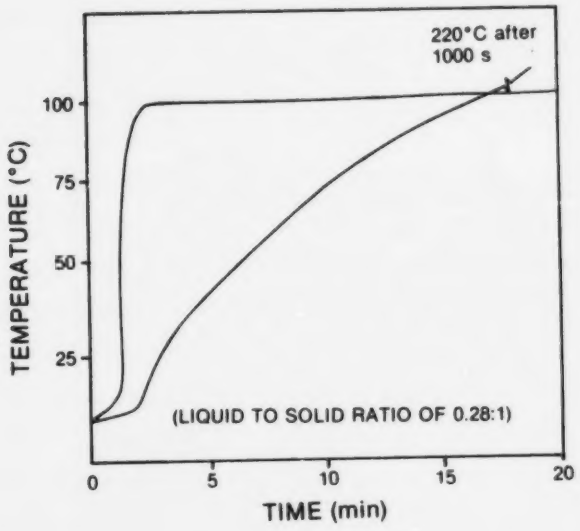

TEMPERATURE RISE (°C)
TIME (min)
SPENT BED; L:S OF 0.5:1 AND 0.25:1
SPENT BED; L:S OF 1:1
SPENT BED; L:S OF 6.67:1
CALCINED LIMESTONE AT 960°C; L:S OF 1.3:1
CALCINED LIMESTONE AT 960°C; L:S OF 4:1

a) Heat releases of AFBC bed waste and of calcined limestone (calcium oxide).

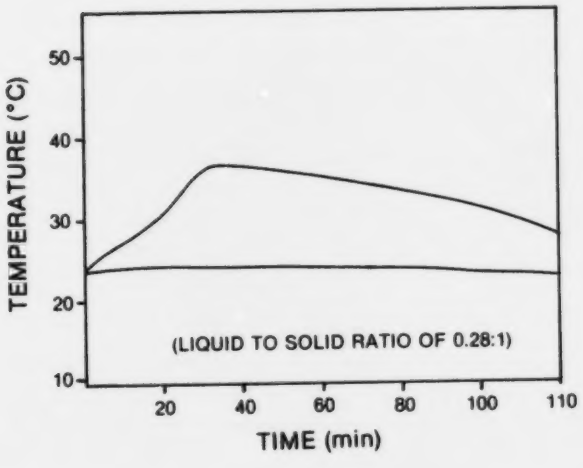

TEMPERATURE RISE (°C)
TIME (min)
CALCINED LIMESTONE; L:S OF 1.3:1
SPENT BED; L:S OF 0.25:1
SPENT BED; L:S OF 0.25:1
SPENT BED; L:S OF 0.25:1
CARRY OVER; L:S OF 0.25:1
CARRY OVER FINES; L:S OF 0.25:1
SPENT BED; L:S OF 0.25.1
CARRY OVER; L:S OF 0.25:1

b) Heat releases of AFBC residues.

FIGURE 7 HEAT RELEASES OF CALCIUM OXIDE, BED WASTES AND CARRY-OVER WASTES AT DIFFERENT LIQUID TO SOLID (L:S) RATIOS (Sun et al., 1978)



a) Two AFBC spent bed materials during slaking.



b) Two AFBC fly ashes during slaking.

FIGURE 8 TEMPERATURE VERSUS TIME FOR TWO SPENT BED MATERIALS AND TWO FLY ASHES DURING SLAKING (Stone and Kahle, 1978)

(1978). The results indicate that the major constituents in the leachates are calcium and sulphate (Table 9). This is consistent with the data presented in Section 2.3.1 which shows that these constituents are present at high concentrations in the solid wastes. The data in Table 9 also indicate that the trace elements aluminum, barium, chromium, molybdenum, silicon and vanadium may be more concentrated in the carryover material leachates than in the spent bed material leachates. This may be due to the higher percentage of coal fly ash, the major source of most readily leachable trace elements in the carryover material, as well as to the greater surface area of the smaller particle sizes. It is interesting to note that leachates from the Site No. 4 "bag filter catch" generally exhibited higher trace element concentrations than leachates from the "cyclone catch" (Table 9). This also suggests that leachability increases with decreasing particle size (CH2M Hill, 1982).

Specific conductance is often used as a general index of total dissolved solids (TDS). A specific conductance of 1.5 mS/cm is generally accepted as being approximately equal to 1000 mg/L of TDS (Sun et al., 1978). Based on this assumption, the TDS concentrations in the bed and carryover leachates reported in Table 9 were in the range of 5200 to 6000 mg/L and 2300 to 4300 mg/L, respectively.

Other test results reported by Sun et al. (1978) indicated that the leachates of mixtures of AFBC spent bed material and fly ash had lower pH, TDS and calcium concentrations than did the leachates of spent bed material alone. The addition of greater than 20% fly ash, by weight, into spent bed material considerably reduced contaminant concentrations in the leachates. This may have been due to pozzolanic reactions occurring between the free CaO in the spent bed material and the SiO_2 and Al_2O_3 in the fly ash when water was added (CH2M Hill, 1982).

From the literature, it appears that the leachability of most trace toxic elements from AFBC spent bed materials is relatively low. This is attributed to the highly alkaline nature of the leachates due to the spent limestone or dolomite in the bed material, which suppresses the dissolution of most heavy metal ions. Copper, zinc, nickel, cobalt, cadmium, lead, manganese and mercury form insoluble compounds under alkaline conditions (Van Der Sloot et al., 1982). Some metals may exhibit a reverse trend at high pH levels; therefore, a highly alkaline leachate does not necessarily guarantee low concentrations of all trace elements which may be of concern at a particular disposal site (CH2M Hill, 1982).

TABLE 9 CHARACTERISTICS OF AFBC RESIDUE LEACHATES (200 hour continuous shake test) (Sun et al., 1978)

	Site No. 1	Site No. 2		Site No. 3		Site No. 4		
Analyte	Carryover	Bed	Carryover	Bed	Carryover	Bed	Cyclone	Bag Filter
Al	< 1	0.05	< 1.0	2	0 to >2	< 1	2	> 2
Ag	< 0.01	< 0.01	< 0.01	< 0.05	< 0.05	< 0.01	< 0.01	< 0.01
As	< 0.003	< 0.002	< 0.002	0.05	< 0.05	< 0.05	< 0.05	< 0.05
B	0.01	< 0.05	0.8	0 to >5	0 to >5	< 0.1	< 0.2	3
Ba	< 1	< 1	< 1.0	< 1	< 2	< 1	2	< 1
Be	< 0.01	< 0.01	< 0.01	< 0.02	< 0.02	< 0.01	< 0.01	< 0.01
Bi	< 0.01	< 0.01	< 0.01	< 0.04	< 0.04	< 0.01	< 0.01	< 0.01
Ca	1184	720	1264	>500	> 50	1276	16	200
Cd	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Co	< 0.01	< 0.05	< 0.05	< 0.01	< 0.01	< 0.02	< 0.02	< 0.02
Cr	< 0.01	< 0.05	< 0.05	< 0.05	< 1.0	0.04	0.3	1.0
Cu	< 0.05	< 0.05	< 0.05	< 0.04	< 0.1	< 0.1	< 0.1	< 0.1
Fe	< 0.05	< 0.1	< 0.1	< 0.3	< 0.3	< 0.1	< 0.2	< 0.2
Hg	< 0.002	< 0.001	< 0.004	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
Mg	< 10	14.4	14.1	< 30	<250	< 1	< 1	1
Mn	< 0.01	< 0.05	< 0.05	< 0.05	< 0.05	< .01	< 0.01	< 0.01
Mo	0.15	0.05	0.2	< 0.11	< 5.0	0.04	0.4	> 2
Na	3	> 5	> 5	0 to >10	0 to >100	4	>> 4	>> 4
Ni	< 0.05	< 0.05	< 0.05	< 0.04	< 0.11	< 0.04	< 0.04	< 0.04
Pb	< 0.01	< 0.05	< 0.05	< 0.05	< 0.05	< 0.01	< 0.01	0.04
Sb	< 0.01	< 0.05	< 0.05	< 0.01	< 0.11	< 0.04	< 0.04	< 0.04
Se	< 0.003	< 0.003	< 0.003	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Si	1	2	> 5	< 2.0	0 to 30	< 0.2	> 2	> 2
Sn	< 0.01	< 0.05	< 0.05	< 1.0	< 1.0	< 0.04	< 0.04	< 0.04
Sr	> 10	> 5	> 5	< 10	0 to >10	4	> 4	>> 4
Ti	< 0.05	< 0.05	< 0.05	< 1	< 2	< 0.05	< 0.05	< 0.05
V	< 0.01	< 0.05	< 0.05	< 0.1	< 1	< 0.02	< 0.03	0.4
Zn	< 1	< 1.0	< 1	< 1	< 1	< 1	< 1	< 1
Zr	< 1	< 0.1	< 0.1	< 1	< 1	< 1	< 1	< 1
SO_4	1247.5	< 10	1410			1350	370	830
S	< 10							
F	< 1					< 1	< 1	< 1
$\underline{Cl}$	12					16	17	148
NO_3 (as N)	10					< 1	< 1	< 1
TOC	10	< 10	< 10			< 10	< 10	< 30
pH	11.9	12.0	12.1			12.0	11.8	10.8
Sp. Cond. (μS/cm)	6470	7850	8060			8930	4780	3440

* all concentrations reported in mg/L unless specified otherwise

2.6 Summary of the Literature Review

While results from the literature are sometimes unclear or difficult to compare, it appears that AFBC wastes are in general, alkaline, permeable, and, depending on their crystalline calcium oxide content, react exothermically with water. Leachates are alkaline and have high TDS levels. Due to the wide variations reported, projections beyond this to specific Canadian situations, cannot be made with any degree of confidence yet. Rather, specific tests of Canadian coal/limestone wastes and wastewaters are now required.

3 THE AFBC WASTE SAMPLE TEST PROGRAM

The physical, chemical, exothermic and leaching properties of three AFBC wastes generated from the combustion of Canadian high sulphur coals in limestone beds, were examined through a variety of tests and analyses. The test procedures evolved with the study. Initially the procedures consisted of methods identified in the literature reviews which had been used for the characterization of pulverized coal combustion wastes. When it became apparent that some methods were unsuitable, they were either deleted or modified. Although quality control procedures throughout the study were more extensive than those normally utilized for known waste types, neither a full description of all of these procedures nor all of the tests, analytical results, and experimental approaches which were tried with these few samples during this investigation, are reported here.

3.1 Source of Samples

Initially, no full-scale AFBC units existed in Canada from which combustion residues could be obtained for analysis and testing. AFBC solid residue samples, however, became available from test burns conducted in 1979 at a U.S. fluidized bed combustion facility operated by Foster Wheeler Development Corporation. The details of this pilot scale testing have been reported elsewhere (Ohmine and Taylor, 1980). The coals and limestone used in these tests were obtained from Canadian sources which were under consideration for use at a new fluidized bed facility at Summerside, P.E.I. The samples were first shipped from the test facility to the CANMET, EMR complex in Ottawa, Ontario. In 1981, the samples obtained from CANMET for a preliminary evaluation of their properties, were identified as follows:

1. Minto Bed Material - Minto coal, wood chip waste and Havelock limestone (fuel was a mixture of 70% Minto coal and 30% wood chips by weight); spent bed material.
2. Devco Bed Material - Devco Prince coal and Havelock limestone; spent bed material.
3. Devco Baghouse Material - Devco Prince coal and Havelock limestone; baghouse wastes.

Table 10 shows the ultimate analysis of the Devco Prince coal and Minto coal/wood chip mixture used during the pilot scale testing (Ohmine and Taylor, 1980). Based on these analyses, these fuels would be classified as high sulphur bituminous

TABLE 10 ULTIMATE ANALYSIS OF COALS USED DURING PILOT SCALE TESTING (Ohmine and Taylor, 1980)

	Devco Prince Coal		Minto Coal/Woodchip Mixture	
Parameter	as received	dry	as received	dry
Carbon	60.06	66.52	52.46	63.51
Hydrogen	4.24	4.69	3.56	4.31
Oxygen	7.31	8.11	3.40	4.10
Nitrogen	1.02	1.13	0.58	0.71
Sulphur	3.95	4.38	6.80	8.24
Ash	13.72	15.17	15.80	19.31
Moisture	9.72	-	17.40	-
Higher Heating Value (MJ/kg)	25.77	28.56	22.05	26.69

Note: all results expressed in percent except where noted

coals. The chemical composition of the Havelock limestone used as the bed material during the tests is given in Table 11 (Ohmine and Taylor, 1980).

3.2 Determination of Physical Properties

Tests were conducted to determine the following physical properties of the residues: moisture content, specific gravity, water holding capacity, permeability, particle size distribution and moisture/density relationships.

The moisture content of each residue was determined in duplicate based on the water loss at 110°C over 24 hours (ASTM D2216-71, 1982). The specific gravity was determined using a pycnometer (ASTM D854-58).

Water holding capacity was determined by placing a sample of residue in a funnel lined with Whatman Number 4 ashless filter paper and covering it with water (Stone and Kahle, 1978). The water was allowed to drain through the sample under the force of gravity until no further drainage appeared for a five minute period. The water retained was determined by oven drying the sample at 110°C for 24 hours.

Falling head permeability tests were performed in duplicate on each solid residue (Soiltest Inc., 1978). Samples were hydrated and then compacted at approximately

TABLE 11 COMPOSITION OF LIMESTONE USED AS BED MATERIAL DURING PILOT SCALE TESTING (Ohmine and Taylor, 1980)

Analyte	Concentration (%)
Silicon	0.88
Aluminum	< 0.01
Titanium	< 0.01
Iron	2.48
Calcium	63.70
Magnesium	0.27
Sodium	0.75
Potassium	1.02
Sulphur	0.05
Phosphorus	< 0.01
Manganese	0.06
Zinc	0.03

20% moisture content in a permeameter similar to the one depicted in Figure 9. The coefficient of permeability was calculated from the equation:

$$K = \frac{QL}{A(h_1-h_0)} \ln(h_0/h_1) \qquad (1)$$

where K = coefficient of permeability, cm/s

Q = flow rate during test, mL/s

L = length of tested residue sample, cm

A = cross-sectional area of permeameter, cm^2

h_0 = height of water column at start of test, cm

h_1 = height of water column at end of test, cm

Particle size analyses were performed on each of the three residues as received using ASTM D422-63. The distribution of particles larger than a No. 200 sieve was determined by sieving approximately 500 g of material through 2.5 cm, 1.9 cm, and No. 4, 10, 20, 40, 60, 140 and 200 sieves. The distribution of particles passing a No. 200 sieve was determined using a hydrometer.

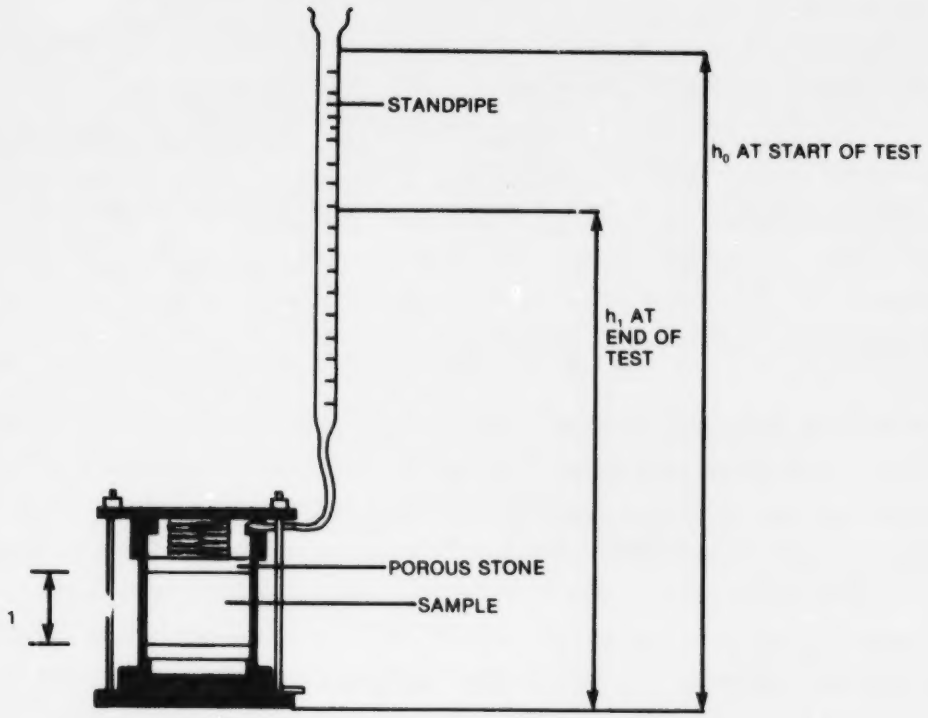


FIGURE 9 FALLING HEAD PERMEAMETER

Moisture/density relationships for each residue were determined in duplicate using ASTM D698-70 Method A. The test involves compaction at various moisture contents into a known volume using a specified force, then determining the density of the compacted specimens.

3.3 Determination of Chemical Properties

Chemical characteristics of the samples were evaluated through determinations of pH and acid neutralization capacity, and application of a detailed analytical program to determine chemical, crystalline and radiochemical composition.

The pH of each residue was determined using a method proposed for measuring soil pH (American Society of Agronomy, 1965). The method involves the addition of 20 mL of 0.01M $CaCl_2$ to 10 g of residue. The pH of the suspension is measured following a 30 minute settling period.

The acid neutralization capacity of each waste was determined by adding a known amount of sample (1 to 2 g) to 20 to 30 mL of water, and titrating with 0.3 N H_2SO_4 while monitoring pH (American Public Health Assoc., 1981). The titration was considered complete when the pH fell below 4.5 and remained so for an indefinite period of time. The baghouse material was tested as received whereas the bed materials were ground in a cylinder mill to a fine powder before testing.

The elemental compositions of the residues were primarily quantified using inductively coupled argon plasma spectroscopy and flame atomic absorption. Elemental analyses were also performed on the different particle size fractions of the two bed materials to determine if relationships existed between particle size and particle composition.

The main crystalline species in the three residues were determined using X-ray diffraction analyses. These analyses were preceded by neutron activation and X-ray fluorescence analyses to identify major elements. For the neutron activation analyses, solid samples were irradiated in a high neutron flux to produce isotopes of the elements present. Element concentrations were determined with a multi-channel gamma spectrometer. Scanning was completed to qualitatively identify elements, followed by quantitative analysis for selected elements. For the X-ray fluorescence analyses, a preliminary analysis for loss on ignition was conducted, followed by quantitative determinations for elements of interest.

The Siemens instrument utilized for the X-ray diffraction analyses used Ca/Ni at 40/20 mA. All recordings were produced under the same conditions of sensitivity and chart speed (1 cm/min; 1 degree/min). An ensemble of peaks was used to establish the presence of each diffracting species, and from the various diffraction peaks produced by each compound, the main peak or one of the main peaks was selected as representative and its intensity measured by the peak height (mm). The selected peaks are shown below.

Compound	Lattice Constant d (A)
$CaSO_4$	3.49 (main)
$CaSO_4 \cdot 2H_2O$	3.06 (2nd most intense)
γ-$CaSO_4$	3.01 (2nd most intense)
CaO	2.40 (main)
$CaCO_3$	3.40 (main)
SiO_2	3.34 (main)

The X-ray diffraction technique only reveals the substances present in crystalline form and not any portions of the substances present in non-crystalline form. Qualitative comparisons and quantitative estimates of the major crystalline species present can be made through calibration with selected crystal species and other techniques such as the previously mentioned X-ray fluorescence. Calibrations with crystalline calcium sulphate were used for determination in this study.

Since combustion processes tend to concentrate elements from the fuels in their wastes, radiochemical constituents were also determined in these wastes by alpha and gamma spectroscopy.

3.4 Determination of Exothermic Properties

The exothermic properties of the residues were examined using standard and nonstandard calorimetry tests, and a bench-scale column procedure developed during the study. Calorimeter tests were used to calculate heats of reaction and to examine temporal changes in temperature at different liquid-to-solid ratios. Column tests were performed to examine spatial as well as temporal changes in temperature in a reacting waste, and to explore the possibility of developing a simple procedure which could be related more directly to anticipated field situations. Some of the initial test methods were discarded after preliminary trials, whereas others were modified and developed. Bomb calorimetry, for example, was discarded whereas column designs went through several changes before a suitable configuration was found.

3.4.1 Calorimeter Tests. Each residue was subjected to a calorimeter test to determine the heat of reaction or loss of enthalpy per unit mass. The procedure used was similar to that described in ASTM C110-76a except for the amounts of water and material used. To a known mass of water contained in a Dewar flask (calorimeter), a known mass of residue was added in a single motion, and the temperature of the well-stirred mixture was followed as a function of time. Two calorimeters of different capacity were used during the testing. The "W" constant or "equivalent in water" of the calorimeters were determined as:

1 litre Dewar flask with 600 g of water:	W = 2.81 kJ/K
0.5 litre Dewar flask with 250 g of water:	W = 1.14 kJ/K
0.5 litre Dewar flask with 300 g of water:	W = 1.35 kJ/K

The heat of reaction per unit mass ($-\Delta H$) was calculated from the temperature increase during the first 30 minutes using the formula:

$$-\Delta H = \frac{W(T_{30}-T_0)}{m} \qquad (2)$$

where: T_0 - temperature in degrees Kelvin at 0 minutes

T_{30} - temperature (K) at 30 minutes

m - mass of sample (kg)

$-\Delta H$ - heat of reaction expressed in kJ/kg

The instantaneous temperature rise in 30 seconds ($T_{1/2}-T_0$) was also calculated.

Calorimeter tests were also used to examine temporal changes in temperature at various liquid-to-solid ratios by continuing to monitor the temperature within a flask until less than a 0.5°C temperature change was observed among three consecutive readings. Deionized water and an acidic medium (pH 4.5) were used to determine temperature-time relationships for the residues at liquid-to-solid ratios of 10:1, 5:1, 3:1 and 1:1. The acidic medium, consisting of 0.045 M sodium acetate and 0.082 M acetic acid, was also used during the serial batch leaching tests previously described.

Similar calorimeter tests were also conducted on different particle size fractions of the spent bed materials. The Minto and Devco bed materials were sieve-sized into four fractions: that retained on No. 10, No. 20 and No. 40 sieves, and that passing the No. 40 sieve. Each of these fractions were monitored for temperature changes in deionized water and the acidic medium at a liquid-to-solid ratio of 1:1.

The precision of the calorimeter procedure was assessed by performing the test in triplicate with industrial grade calcium oxide and comparing the results with those given in the literature.

3.4.2 Column Tests. Column testing was initiated to permit examination of exothermic properties in a larger dynamic system which might approximate anticipated landfill disposal situations better than the smaller calorimeter tests. There are no standard protocols for this type of testing. The first test column tried was a 2.54 cm (inside diameter) polyvinyl chloride (PVC) pipe. This pipe deformed (i.e., violent reaction) and was replaced by an insulated Schedule 40 PVC pipe which also deformed during the initial test series.

The third column design did not fail in the initial tests and was subsequently used in the test battery. This column consisted of an 8 cm diameter stainless steel tube, 40 cm in height, which was lined with a teflon sleeve and fitted with 5 dial thermometers. Thermometer 1 was located about 4 cm below the surface of the material in the column. Thermometers 2 to 5 were positioned at 4 cm intervals downward in the column. The column was covered with fiberglass insulation and held vertically in a retort stand. A wire mesh screen covered the bottom of the column. Deionized water or the acidic medium was added to the top of the column at a rate of 1.24 mL/min which is equivalent to a precipitation rate of 1.6 cm/h. The top of the column was filled with a layer of glass beads in order to help distribute the flow evenly over the surface of the material. Temperatures at the five positions were recorded at 5 minute intervals. Monitoring continued until approximately 45 minutes after detection of a peak in the bottom thermometer. Leachates from the column were also analyzed for gross parameters to allow comparisons with the batch leaching test results.

It must also be noted that one attempt was made to determine a reference calcium oxide reaction response by adding water to industrial grade calcium oxide in the test apparatus. The ensuing reaction was immediate and extremely violent. Fortunately there were no injuries and no further column tests with a calcium oxide reference were attempted.

3.5 Determination of Leaching Properties

Leachability tests can indicate if environmental problems may be expected from a waste coming in contact with water during handling, transport and disposal. Leachates can also be used to explore pollution control alternatives such as the practicability of chemical and physical wastewater treatments. Several different leaching protocols have been developed or suggested for studies of this nature. A recently developed serial batch leaching procedure was selected for these tests (Côté and Constable, 1982).

The wastes were leached for 10 cycles (Devco bed material) or 20 cycles (Minto bed and Devco baghouse materials) using distilled water and an acidic medium at 4:1 and 20:1 liquid-to-solid ratios. After each 18-hour leaching cycle, the undissolved solids were separated from the leachate by centrifugation followed by filtration through 0.45 µm filter paper. The solids were then contacted with fresh leaching medium for the next leaching cycle. Conductivity, pH and total dissolved solids (TDS) concentrations were measured in the leachates after every cycle. Chemical analyses were conducted on

the Devco bed leachates from Cycles 1, 4 and 10, and on the Minto bed and Devco baghouse leachates from Cycles 1, 2, 4, 6, 10, 15 and 20. The undissolved solids remaining at the end of the tests were subjected to elemental analyses.

3.6 Quality Controls

The atmospheric fluidized bed combustion process is now being developed for large-scale combustion applications in the megawatt power class. The solid residues from operations of this size have not been well characterized though, and optimum methods for their analysis have yet to be determined and verified. In consideration of this, several different analytical methods were used and a detailed quality control program was followed for the solid and leachate analyses to ensure that the methods provided acceptable results.

For the leachate quality control program, previously analyzed leachate samples were spiked with known concentrations of selected elements and resubmitted for analysis. Thirteen elements were selected, and were spiked based on the minimum and maximum concentrations observed in the leachates. The selection of leachates and spiked elements was somewhat restricted because of the limited volumes of leachate available. The Devco baghouse leachates were used most often for spiking because they contained the highest concentrations of analytes.

A standard reference material of AFBC solid waste was not available; however, a standard reference PCF fly ash was included in the solid material quality control program. The AFBC residues were not anticipated to have the same glass-like properties as fly ashes from conventional pulverized coal-fired processes, therefore, they were expected to be more readily digestable during analytical determinations. The accuracy of the AFBC solid analyses was anticipated to be at least as good as that of the fly ash analyses, provided that there were no procedural interferences.

The use of this reference PCF material permitted a comparison of the known requirements for PCF wastes analysis with those for FBC residue analysis as well as the direct comparison of the compositions of the PCF and AFBC ash residues.

As indicated in other sections, replicate analyses and/or method comparisons were also employed in other testing.

4 RESULTS AND DISCUSSION

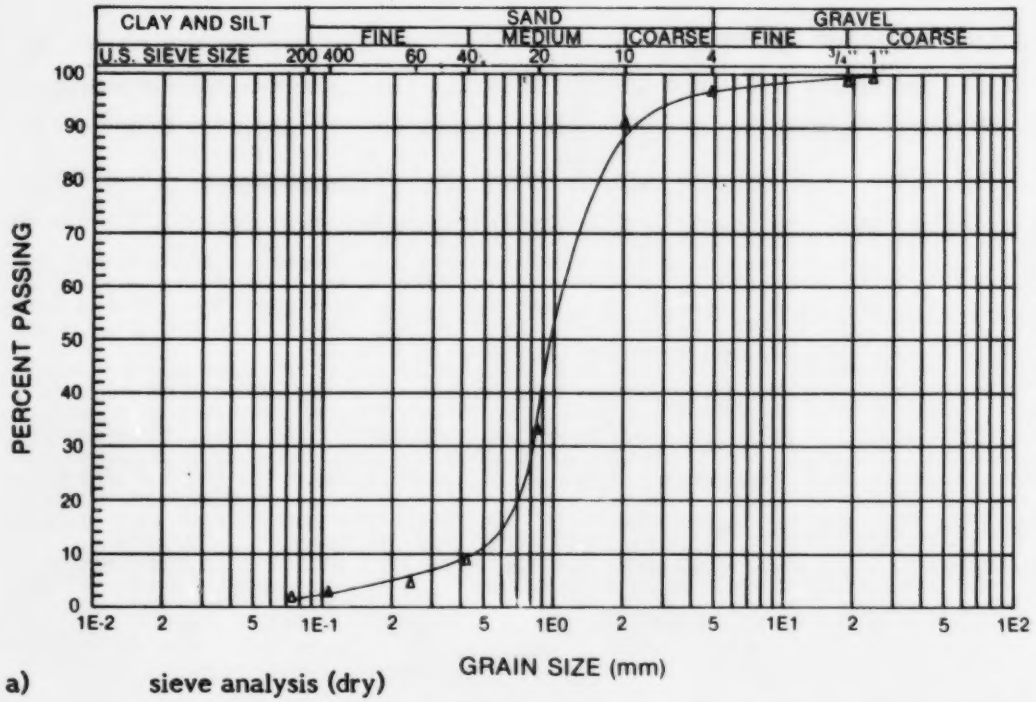
4.1 Physical Properties

The three solid residues had different physical appearances. The Devco baghouse material was a fine powder which was light grey-brown in colour. The Devco bed material was composed mainly of fine greyish-white granules with larger brown and grey particles. The Minto bed material contained the largest size particles. It was dark grey-brown in colour and contained numerous large dark granules.

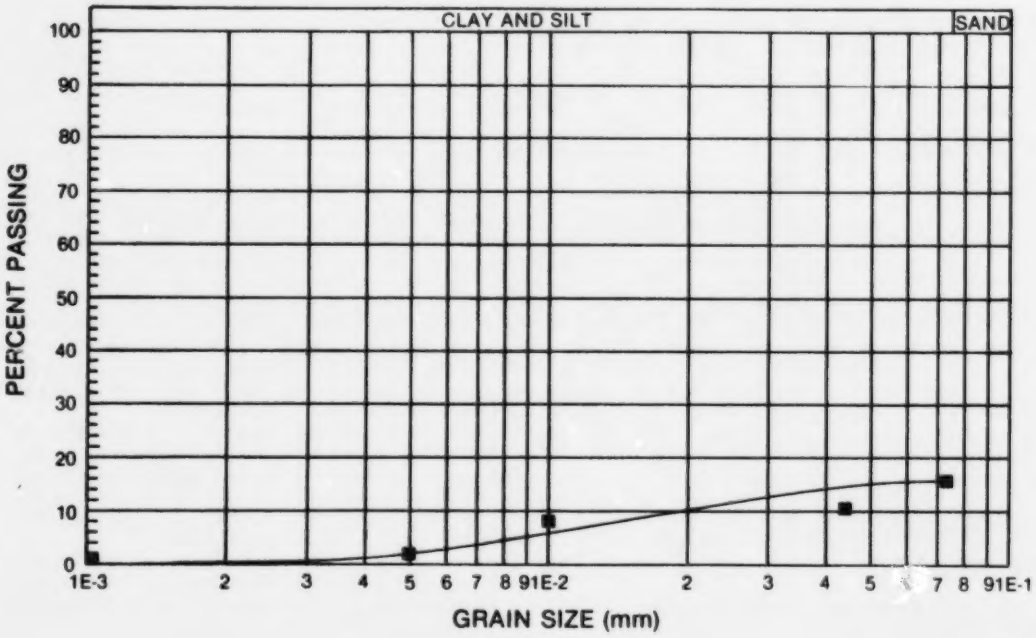
In preliminary sieve sizing comparisons between slaked and unslaked materials, it appeared that slaking affected some particle size fractions significantly. For example, the percentages of unslaked Devco bed materials passing the number 60, 140 and 200 sieve sizes were 15.6, 10.1 and 1.1 respectively. In comparison the percentages of the same material passing the same sieve sizes after slaking, were 35.2, 29.6 and 28.0 respectively. For the Devco baghouse material only 16.9% of the unslaked material passed the number 200 sieve while 89.8% passed after slaking. The unslaked particle sieve size results are shown in Figures 10 to 12.

Although the smallest particle fraction (hydrometer results for particles passing the number 200 sieve) are also shown, these results do not appear to be of much value as a measure of fresh dry material sizes other than for comparison with those reported by other researchers who used this method. The slaked and unslaked results for the larger particle sizes mentioned above indicate that water affects some particles significantly. The leaching tests indicated these materials are water soluble and the calorimetry also indicated strong reactivity with water. Since the hydrometer procedure involved the dispersion of the solids in water, it is unlikely that the properties and sizes of some of the particles did not change during the hydrometer test. The procedure also requires the addition of sodium metaphosphate as an anti-coagulant and of sodium carbonate to maintain pH between 8 and 9. During the hydrometer analysis of the Devco baghouse sample, a gel formed above the ash suspension, which hindered particle sizing. This procedure, therefore, is not reliable for particle sizing of dry AFBC residues of the type examined in this study. It appears that other AFBC ash materials which were reported to have been successfully examined using this method, had considerably different chemical characteristics than the materials examined here.

The average results of the moisture content, specific gravity, water holding capacity and permeability tests are shown in Table 12. The moisture contents of both bed

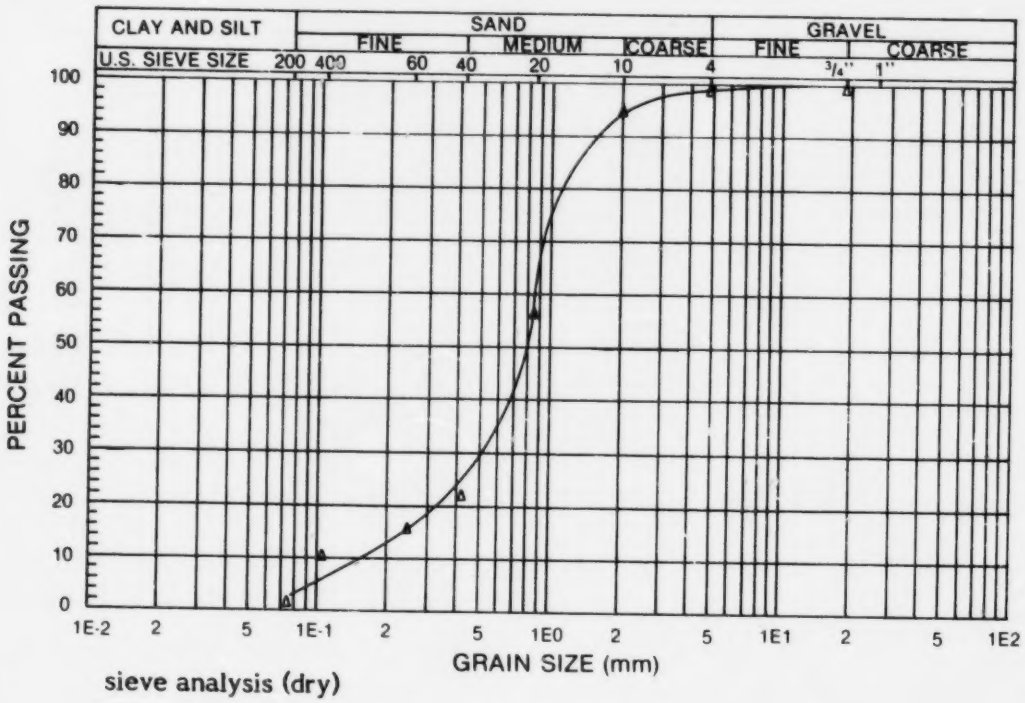


a) sieve analysis (dry)

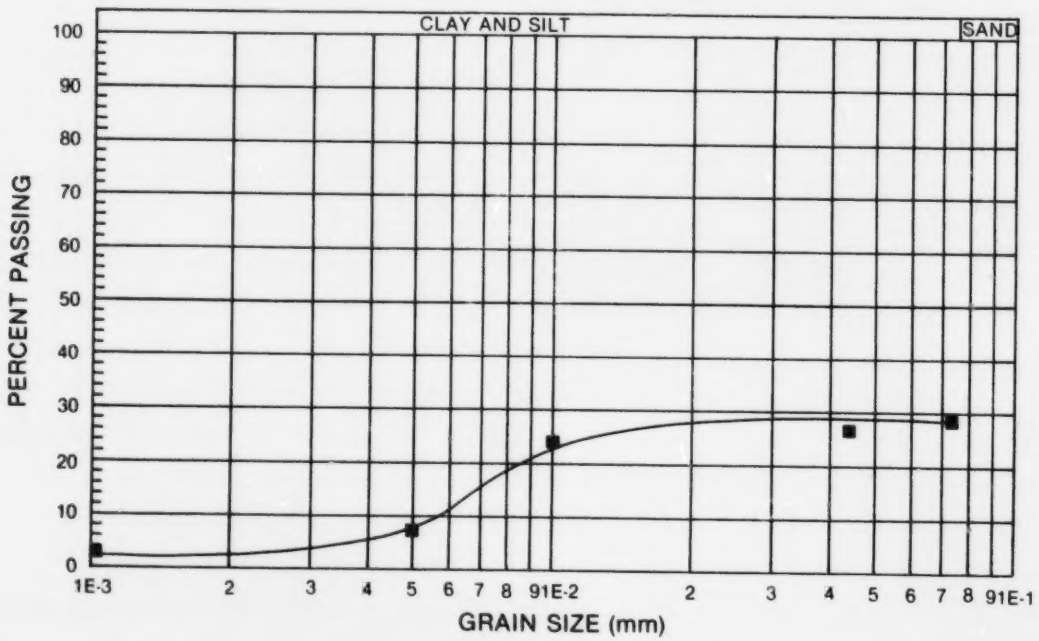


b) hydrometer analysis (slaked)

FIGURE 10 PARTICLE SIZE DISTRIBUTION OF MINTO BED MATERIAL

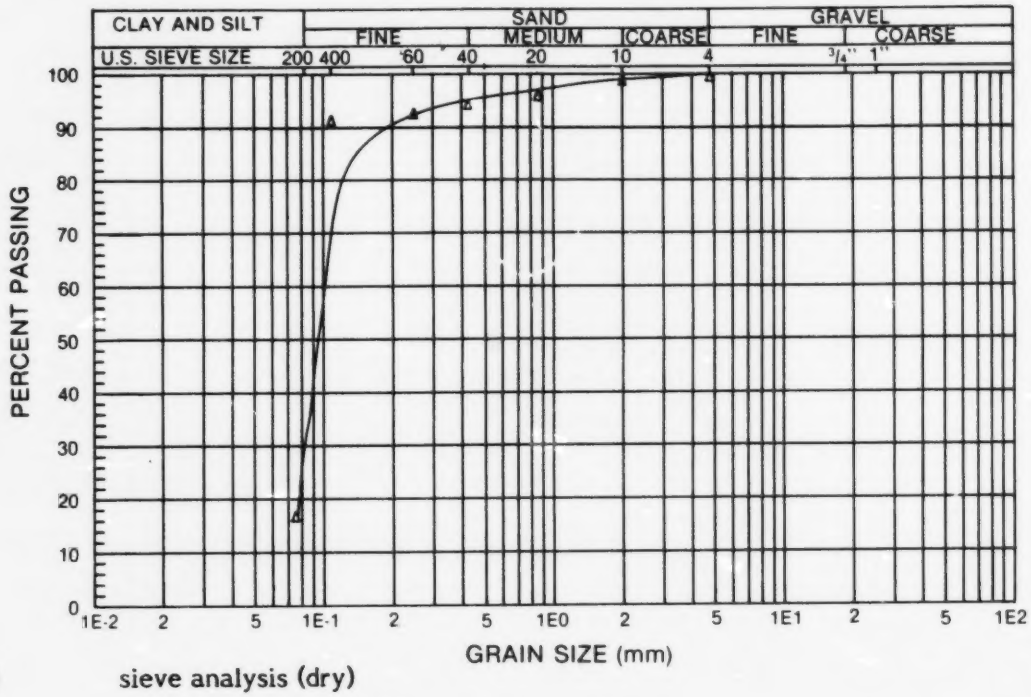


a) sieve analysis (dry)

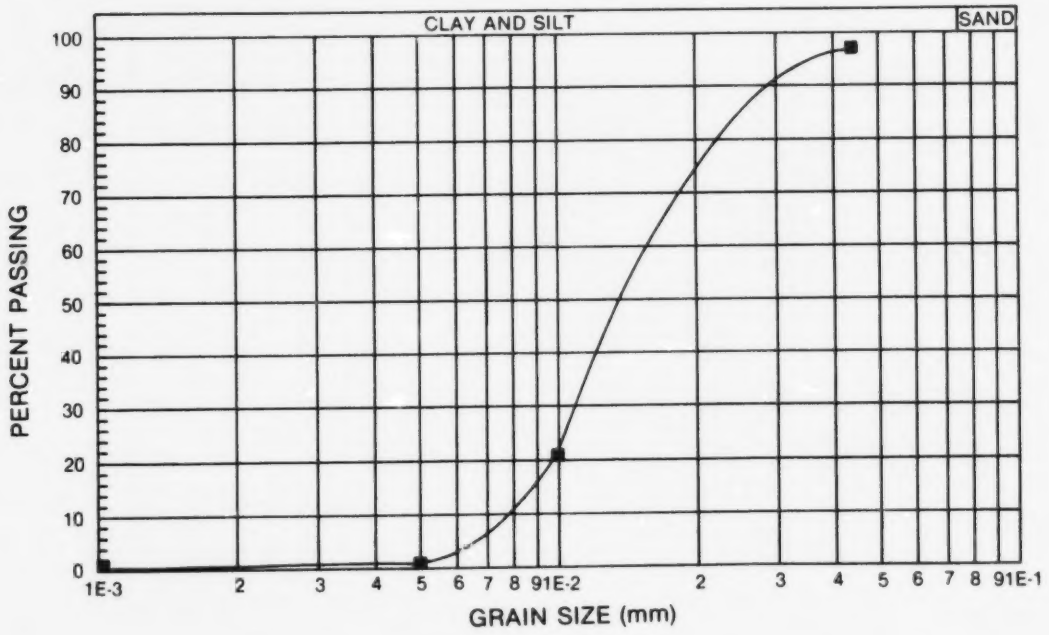


b) hydrometer analysis (slaked)

FIGURE 11 PARTICLE SIZE DISTRIBUTION OF DEVCO BED MATERIAL



a) sieve analysis (dry)



b) hydrometer analysis (slaked)

FIGURE 12 PARTICLE SIZE DISTRIBUTION OF DEVCO BAGHOUSE MATERIAL

TABLE 12 PHYSICAL PROPERTIES OF THE THREE AFBC RESIDUES

Parameter	Minto	Devco	
	Bed	Bed	Baghouse
Moisture Content (%)	0.0	0.1	5.4
Specific Gravity at 20°C (g/cm^3)	2.82	2.93	2.80
pH (units)	12.1	12.2	10.8
Water Holding Capacity (%)	48	63	145
Permeability (cm/s)	2.2×10^{-2}	2.5×10^{-2}	3.3×10^{-5}

materials were very low, at 0.0% and 0.1% for the Minto and Devco bed materials, respectively. The moisture content of the Devco baghouse material, however, was significantly higher at 5.4%. Whether this occurred through accidental wetting or absorption of moisture from the air during storage is not known. Since the residues were in storage for more than two years prior to the start of this characterization program, and it is unlikely that their containers were always sealed during this time, there was probably opportunity for humidification and/or carbonation of at least some of the samples as a result of exposure to the atmosphere. It is probable that these residues, especially the baghouse material, exhibited somewhat different properties than those of fresh samples.

The specific gravities of the three residues ranged between 2.80 and 2.93 g/cm^3. These values compare favorably with those of 2.65 and 2.80 g/cm^3 reported by Stone and Kahle (1978) for an AFBC fly ash and bed material, respectively. For comparison, an average value for soils is about 2.65.

The average water holding capacity of the Devco baghouse material was much higher at 145% than the Minto and Devco bed materials at 48% and 63%, respectively. Since this test indicates the amount of moisture which is retained by a material under the force of gravity, these results suggest that the baghouse material is much less drainable than the bed materials. If disposed of separately, it might require different disposal design considerations since it is likely to retain a high moisture content for an extended period of time even if drainage is provided. It also appears that the larger bed materials may continue to change with contact with water or the atmosphere over time.

The coefficients of permeability of the two bed materials were approximately the same at about 2.4×10^{-2} cm/s, and are at the upper limit of the range of 3.7×10^{-2} to 6.6×10^{-4} cm/s for AFBC spent bed materials (Stone and Kahle, 1978). The coefficient of permeability of the baghouse material, at 3.3×10^{-5} cm/s, was three orders of magnitude less than that of the bed materials, and is less than the value of 1.9×10^{-3} cm/s for AFBC carryover/fly ash (Stone and Kahle, 1978). For comparison, materials which have permeability coefficients in the range of 10^{-2} cm/s are classified as moderately permeable.

Preliminary results for compaction testing indicated that a maximum dry density was not reached for the Devco baghouse material up to and beyond 70% moisture content. In comparison, most clays achieve maximum density below 30% moisture content. The bed materials appeared to reach their maximum densities in the 20% to 25% moisture content range and achieved somewhat higher densities than the baghouse material but these figures were significantly lower than those achieved by most silts and clays with comparable moisture contents. As noted with the hydrometer analyses, this test may not be completely appropriate for highly reactive materials of this type, as particle size reductions and chemical reactions may continue to occur throughout the tests. Although these test results were questionable and are not reported in detail, they do suggest that initially, the bed and baghouse materials are very different in terms of the amounts of water they require to maximize their densities and thereby minimize their disposal area requirements.

4.2 Chemical Properties

4.2.1 pH and Acid Neutralization Capacity. The pH values of the bed materials were approximately equal at 12.1 and 12.2 for the Minto and Devco samples, respectively. The pH of the Devco baghouse material was 10.8. This indicates the residues are very alkaline, even in comparison with very alkaline PCF ashes. Leachates produced through water contact would also be expected to have very high pH values. This was verified in the leachability tests (Section 4.4).

The acid neutralization capacity of both bed materials was 9 gram-equivalents of 1 N H_2SO_4 per kilogram of residue. This is within the range of 2.6 to 26 gram-equivalents/kg determined by Stone and Kahle (1978) for two AFBC spent bed materials. The bed materials in this study were ground prior to acid neutralization testing whereas those reported by Stone and Kahle were not. Grinding may have increased the measured capacities above those that would have been observed if the samples had been tested as

received. However, grinding probably gave an indication of the total capacities of the residues to neutralize acid, since performing the short-term tests on unground samples would have neglected the slow diffusion of alkali from the interior of the particle matrix (Houle and Long, 1980) and the continuing dissolution of the particle with time. The rates of these reactions would likely also be dependent on particle morphology.

The neutralization capacity of the Devco baghouse material, at 2.7 gram-equivalents/kg, was lower than the bed material and below the range of 8.8 to 17.5 gram-equivalents/kg reported by Stone and Kahle (1978) for two AFBC fly ashes.

4.2.2 Chemical Composition. The elemental compositions of the residues were quantified using inductively coupled argon plasma (ICAP) spectroscopy and flame atomic absorption (AA). Neutron activation (NAA) and X-ray fluorescence (XRF) analyses were also performed for some elements with the X-ray diffraction (XRD) analyses to assist in the determination of major crystalline species. There was good agreement between the various elemental analysis techniques. The elemental composition results for the solids are shown in Table 13. Compositions of different particle size fractions are provided in the Appendix.

Based on X-ray diffraction analyses conducted on a PCF fly ash during the preliminary investigation stage of this study, calcium oxide appeared to be essentially absent from significant amounts of calcium substances contained in PCF residue. The calcium was indicated to be in other forms and species, most probably in calcium-aluminum-silica matrices. In contrast, calcium oxide in the crystalline form was the major form of the calcium in the AFBC residues examined for comparison.

Further examinations of the crystalline species were conducted with XRD analyses and the XRF and NAA analyses previously discussed. Since the X-ray diffraction technique does not detect non-crystalline or amorphous fractions directly, other methods must be utilized in conjunction with XPD to indicate whether such fractions are present. Comparison of the pure $CaSO_4$ anhydrite results with those of the samples showed that the amorphous component was a small fraction of the overall mass. Calibration with $CaSO_4$ was performed in order to help obtain quantitative results for the major crystalline species of interest. Although an unequivocal composition of the residues is not provided by this method, the major crystalline species composition can be identified and, in combination with results obtained by other methods, a relatively accurate estimate of the forms and quantities of the substances of interest may be constructed. Based on these analyses and calculations, the probable distributions of calcium in the bed material samples are estimated to be as follows:

TABLE 13 CHARACTERIZATION OF AFBC SOLIDS BEFORE LEACHING

Parameter/Material	Minto Bed	Devco Bed	Devco Baghouse
Aluminum	81 600	30 300	76 300
Antimony	< 100	< 100	< 100
Arsenic	176	120	308
Barium	130	65	365
Beryllium	0.27	< 0.05	8.35
Boron	94	86	183
Cadmium	4	5	5
Calcium	293 000	387 000	160 000
Total Carbon	4 000	3 000	38 000
Chromium	14	10	136
Cobalt	< 5	< 5	< 5
Copper	15.4	10.8	116
Iron	12 700	14 600	116 000
Lead	5	35	240
Lithium	40	40	130
Magnesium	4 920	2 820	7 150
Manganese	398	483	452
Molybdenum	< 30	< 30	180
Nickel	28	27	144
Phosphorus	1 530	390	1 230
Potassium	7 700	3 700	12 000
Silicon	107 000	48 300	90 100
Silver	0.7	0.7	< 0.5
Sodium	8 300	2 600	19 800
Strontium	162	150	775
Thallium	17.4 ± 2	20.6 ± 3	15 ± 3
Thorium	9.3	2.9	12
Titanium	585	845	4 260
Uranium	5.2	2.2	4.2
Vanadium	11.7	16.3	194
Zinc	49	31	154
Zirconium	57	26	87
Mercury	< 0.05	2.05	< 0.05
Total CN^-	< 0.1	< 0.1	< 0.1

Note: results in µg/g unless otherwise indicated

Calcium Species Percent Composition

Material	$CaSO_4$	CaO	$CaCO_3$
Minto Bed	3.4	33.8	5.2
Devco Bed	6.8	37.7	11.3

These calcium oxide contents are supported by the preliminary XRD assessment. They indicate that the convention of reporting elemental calcium contents as only CaO is not entirely appropriate for AFBC wastes, and may not be appropriate for other combustion wastes either since the actual CaO content may be important in determining the waste characteristics.

Diffraction spectra did not indicate the presence of more than a trace of $AlSO_4$. Since it also appeared that some of the sulphur was not present as calcium sulphate ($CaSO_4$), it was concluded that some sulphur was present in either crystalline or amorphous elemental forms. This unusual conclusion received unexpected support from another analytical study which included samples of the same AFBC wastes and reported the presence of elemental sulphur. These observations of the presence of elemental sulphur are contrary to the assumption commonly made for AFBC residues, that all sulphur is present as sulphate and that all sulphate is present in combination with calcium. This was also surprising since it suggests that the bed was not well mixed during combustion and that areas of reducing conditions may have been present. An alternative hypothesis is that reactions continued to occur in the spent waste material after combustion, resulting in the breakdown of calcium sulphate over time. Consequently, the actual amounts of calcium oxide, calcium sulphate and calcium carbonate as well as other calcium species may all be of interest in AFBC waste and similar combustion waste studies.

The results of the alpha and gamma spectroscopy analyses for naturally occurring radioactive substances are given in Table 14. These indicate that, like other coal combustion residues, low concentrations of natural radionuclides are present in these wastes and their concentrations will be determined primarily by the contents in the feed materials.

4.3 Exothermic Properties

The exothermic properties of the residues were investigated through calorimeter tests to determine heats of reaction and examine temporal changes in temperature

TABLE 14 RADIOCHEMICAL ANALYSES OF THREE AFBC SOLID RESIDUES

	Minto	Devco	
Analyte	Bed	Bed	Baghouse
U 238	0.10	0.08	0.04
Th 234	0.10	0.07	0.05
Pa 234	0.10	0.07	0.05
U 234	0.10	0.07	0.05
Ra 226	0.11	0.10	0.03
Bi 214	0.11	0.13	0.03
Pb 210	0.20	0.12	<0.015
Pb 214	0.11	0.07	0.02
Th 232	0.035	0.07	0.015
Ra 228	0.035	0.07	0.015
Ac 228	0.035	0.07	0.015
Th 228	0.035	0.07	0.015
Ra 224	0.035	0.07	0.015
Daughters Rn 220	0.036	0.07	0.016

Note: all results are expressed in Bq/g

at different liquid-to-solid ratios. Column tests were used to examine spatial as well as time/temperature variations at different residue depths in the column. The performances of different column configurations were also of interest from a test apparatus development perspective.

4.3.1 Heats of Reaction. The heat of reaction or loss of enthalpy per unit mass ($-\Delta H$) of each residue was determined by slaking the residues in a Dewar flask at different liquid-to-solid ratios, measuring the temperature increase during the first 30 minutes, and calculating $-\Delta H$ using Eq. (2) (Section 3.4.1). It was originally planned to slake the three materials at liquid-to-solid ratios of 1:1, 3:1, 5:1 and 10:1; however, the reactivity of the Devco baghouse material was almost negligible and this material was dropped from further heat release testing after one confirmatory run at the 1:1 ratio. Since this sample had a moisture content of 5.4% when received, heat release may have occurred before testing began.

Two sets of Minto and Devco bed material samples were slaked. Additional care was taken with the second set of samples to avoid unnecessary contact with air, which might have decreased the reactivity by humidification and carbonation.

The results of the heat of reaction determinations are given in Table 15. Also shown are the temperature increases during the first 30 seconds and the first 30 minutes. Temperature rise in the bed materials during the first 30 seconds was about 20% of the total temperature rise during the 30 minute test, but was essentially complete after 30 seconds in the Devco baghouse test. Temperature increases were greater at the lower liquid-to-solid ratios.

The precision of the calorimeter procedure was assessed by performing the test in triplicate with industrial grade "quicklime" (CaO) and comparing the temperature-time curves with those given by Kunesh (1976) and Boynton (1966). The results shown in Figure 13, indicate that the procedure is reproducible.

The heats of reaction of the Minto bed material ranged between 112 and 132 kJ/kg in the six tests, and averaged 124 kJ/kg. The heats of reaction of the Devco bed material ranged between 29 and 56 kJ/kg, and averaged 38 kJ/kg. The additional care taken during the second set of tests to avoid air humidification gave inconclusive results, since temperature increases were greater in the second set of tests with the Minto bed materials, but were less with the Devco bed materials. The heat of reaction of the Devco baghouse material, 14 kJ/kg, was about three times less than that of the Devco bed material. This value, however, may not be representative of fresh (i.e., dry) material.

The exothermic reactions of the residues appears to have been primarily attributable to calcium oxide slaking (Section 2.3). The large difference between the heats of reaction of the two bed materials (124 kJ/kg for Minto versus 38 kJ/kg for Devco) cannot be explained by their CaO contents alone. The CaO contents of the two residues were almost the same at 34% and 38% for the Minto and Devco bed materials respectively. The difference between the heat of reaction determinations of the two materials could be due to several reasons. For example, the exothermic properties of the samples might have changed due to reactions with the atmosphere during storage handling. Another possibility is that substances other than CaO also contributed to heat release. These could be present in different proportions in the residues because different coals were used and wood chips were combusted with the Minto coal. Fresh samples of similar materials and, perhaps, additional or different test procedures, are indicated for further study.

TABLE 15a CALORIMETRY RESULTS USING THE FIRST SUBSAMPLE OF MATERIAL

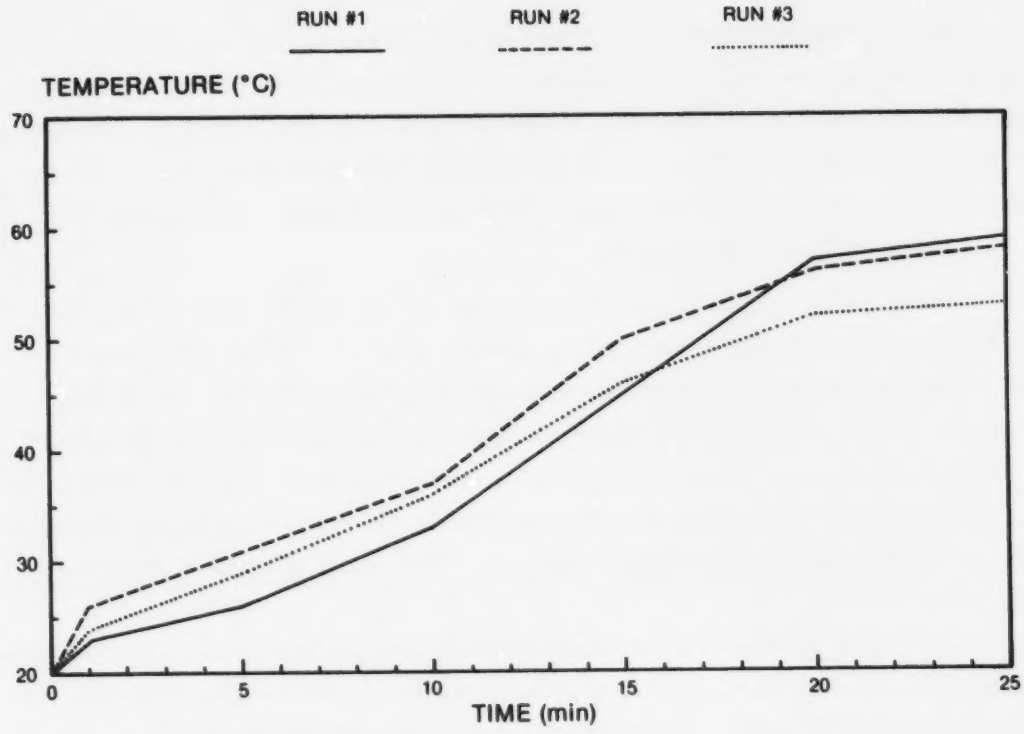
Test No.	Sample	Mass of Water (g)	Mass of Sample (g)	Mass Ratio Water Sample	$T_{1/2}-T_0$ (K)	$T_{30}-T_0$ (K)	$-\Delta H_{30}$ (kcal/kg)	$-\Delta H_{30}$ (kJ/kg)
1	Minto Bed	600	60	10	0.45	2.4	26.8	112
2	Minto Bed	600	120	5	0.6	5.1	28.5	119
3	Minto Bed	250	83	3	0.5	9.35	30.6	128
4	Devco Bed	600	60	10	0.2	1.2	13.4	56
5	Devco Bed	600	120	5	0.25	1.65	9.2	39
6	Devco Bed	250	83	3	0.15	2.55	8.4	35
7	Devco Bag-house	600	60	10	0.2	0.3	3.3	14

TABLE 15b CALORIMETRY RESULTS USING THE SECOND SUBSAMPLE OF MATERIAL

Test No.	Sample	Mass of Water (g)	Mass of Sample (g)	Mass Ratio Water Sample	$T_{1/2}-T_0$ (K)	$T_{30}-T_0$ (K)	$-\Delta H_{30}$ (kcal/kg)	$-\Delta H_{30}$ (kJ/kg)
8	Minto Bed	300	30	10	0.45	2.92	31.4	131
9	Minto Bed	300	60	5	1.3	5.85	31.5	132
10	Minto Bed	300	100	3	1.7	8.9	28.7	120
11	Devco Bed	300	30	10	0.17	0.87	9.4	39
12	Devco Bed	300	60	5	0.25	1.25	7.0	29
13	Devco Bed	300	100	3	0.35	2.25	7.3	31

TABLE 15c BEST VALUES FOR CALORIMETRY

Sample	$-\Delta H$ (kcal/kg)	$-\Delta H$ (kJ/kg)
Minto Bed	31.5	132
Devco Bed	8.2	34
Devco Baghouse	3.3	14



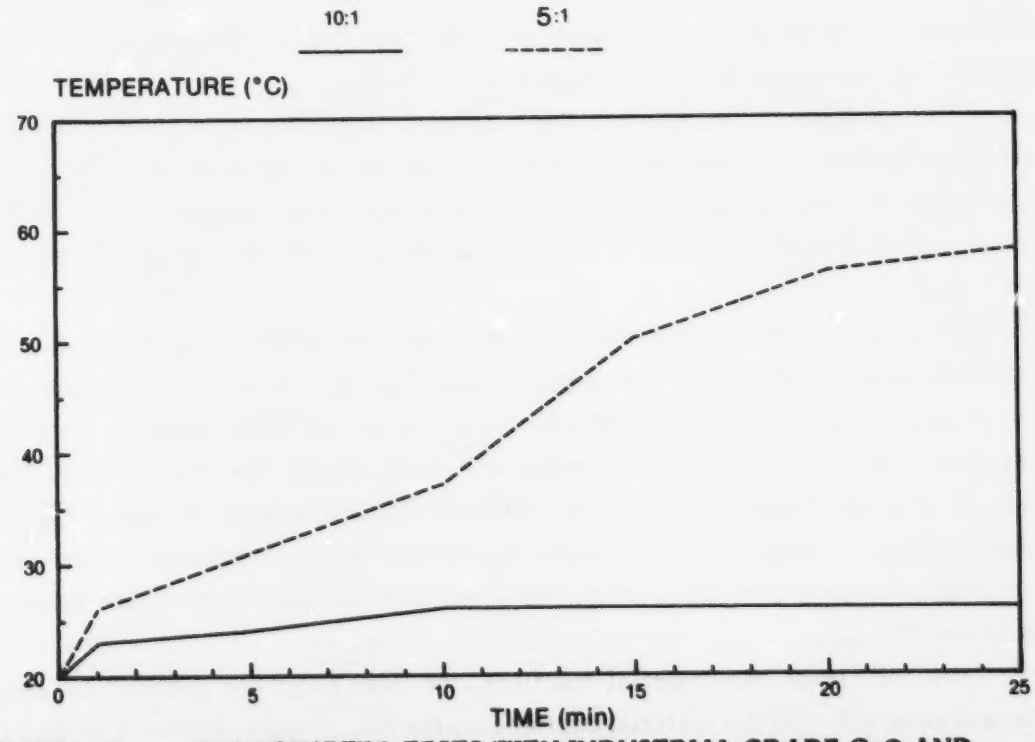


FIGURE 13 CALORIMETER TESTS WITH INDUSTRIAL GRADE CaO AND DISTILLED WATER MEDIUM, TEMPERATURE VERSUS TIME

From a handling and disposal perspective, it is not only significant that these samples are reactive but that they continued to remain reactive after several years of storage. It is also of concern that the reasons for and the significance of, the observed differences are not clear. The ability to predict the conditions under which reactions of this nature might occur in field situations, may be of considerable importance.

4.3.2 Extended Calorimeter Tests

Temporal variations in temperature past the 30-minute time period used in the standard calorimeter test were examined by continuing to monitor the tests until less than a 0.5°C temperature change was observed three consecutive readings. In addition, four liquid-to-solid ratios (1:1, 3:1, 5:1 and 10:1) and two liquids (deionized water and the acidic medium used in the leaching tests) were used. The tests were only conducted on the two bed materials because of the almost negligible exothermic nature of the baghouse material and a shortage of this sample material. The results of these tests are shown in Figures 14 and 15.

As found in the heat of reaction tests, temperature rises were inversely related to liquid-to-solid ratio, and were greatest in the Minto bed material. The rate of temperature increase was also faster in this material, as particularly evident in Figure 16. The rate of increase was faster at the higher liquid-to-solid ratios as well. Both bed materials showed slightly greater temperature rises with the acidic medium than with deionized water, particularly at higher liquid-to-solid ratios.

The results also indicate that the exothermic reactions were close to completion after 30 minutes, but that temperatures continued to increase past this time, particularly at the 1:1 liquid-to-solid ratio. Problems were encountered with the calorimeter test procedure at this ratio, since a viscous paste was formed which was very difficult to mix.

Similar extended calorimeter tests were also conducted on different particle size fractions of the two bed materials, using deionized water and the acidic medium at a liquid-to-solid ratio of 1:1. Tests could only be conducted on three of these fractions: those captured on the No. 20 and 40 sieves and that passing the No. 40 sieve (pan material). The material captured on the No. 10 sieve was too large to be used in the test apparatus, as large particles tended to shatter the vacuum bottle liner of the Dewar flask during mixing. Temperature variations in the three particle size fractions are shown in Figures 16 and 17.

For the Devco bed material fractions, the most rapid and greatest temperature rise was observed with the material captured on the No. 20 sieve, followed by that on

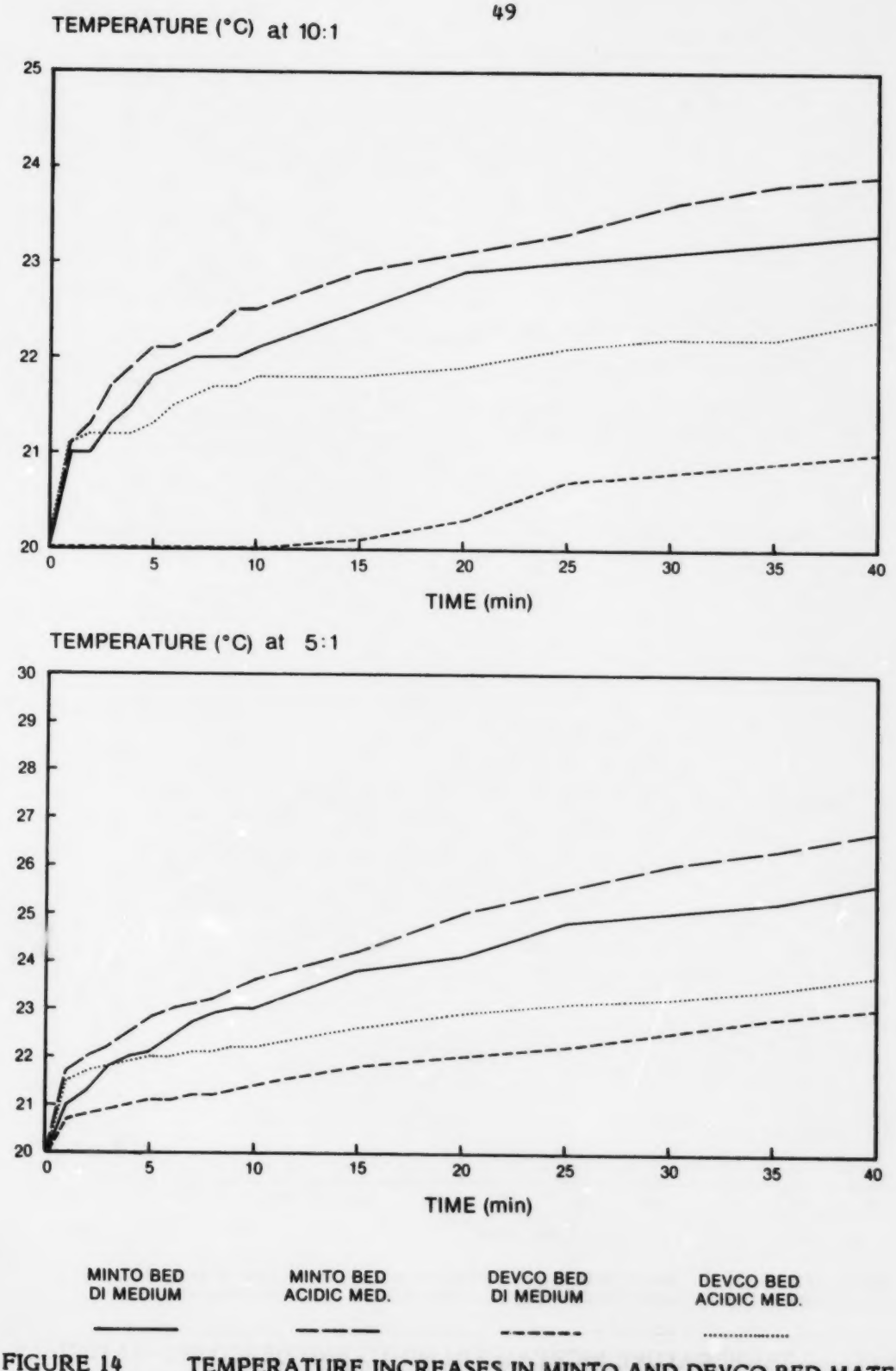


FIGURE 14 TEMPERATURE INCREASES IN MINTO AND DEVCO BED MATERIALS AT 10:1 and 5:1 LIQUID TO SOLID RATIOS

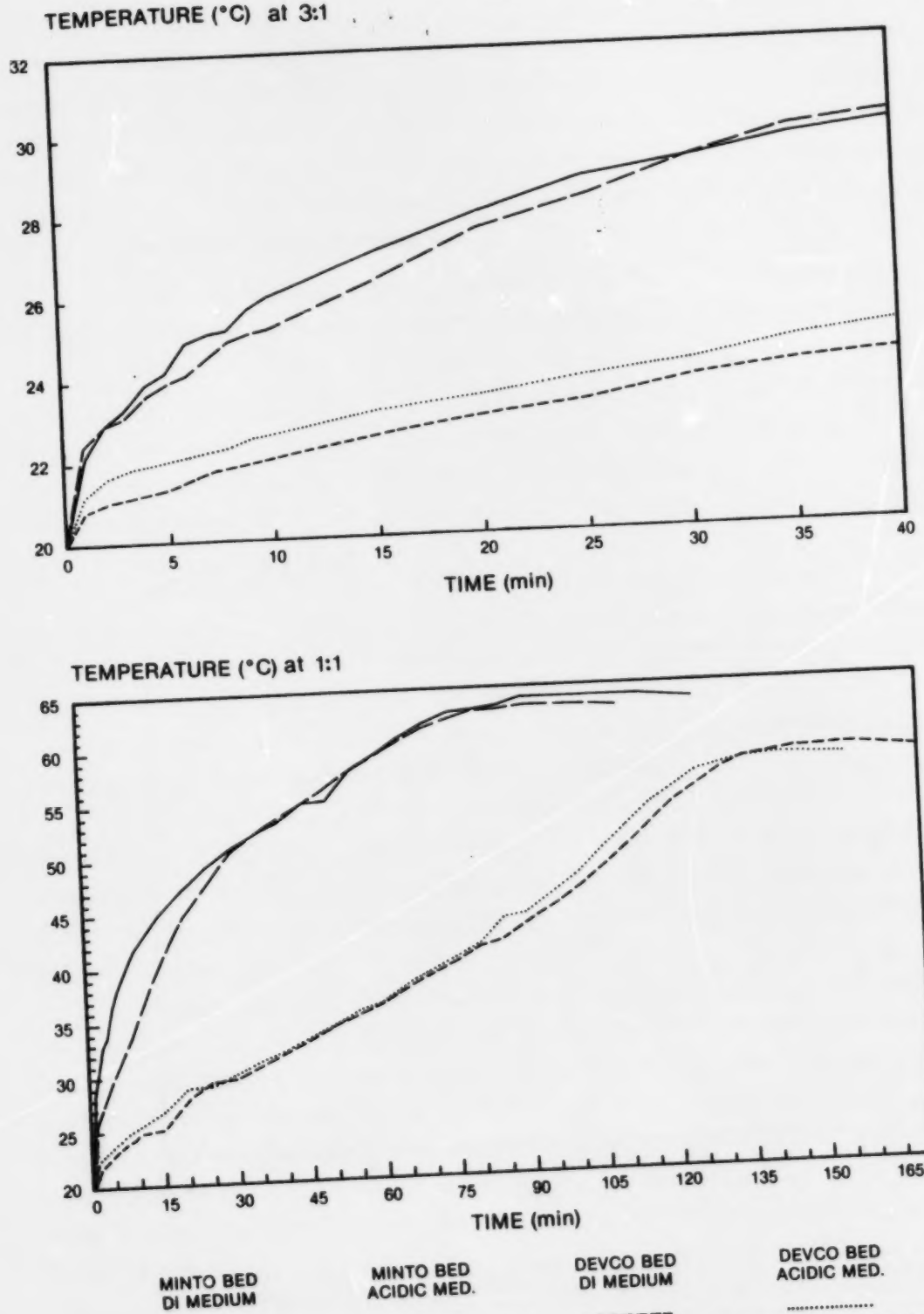


FIGURE 15 TEMPERATURE INCREASES IN MINTO AND DEVCO BED MATERIALS AT 3:1 and 1:1 LIQUID TO SOLID RATIOS

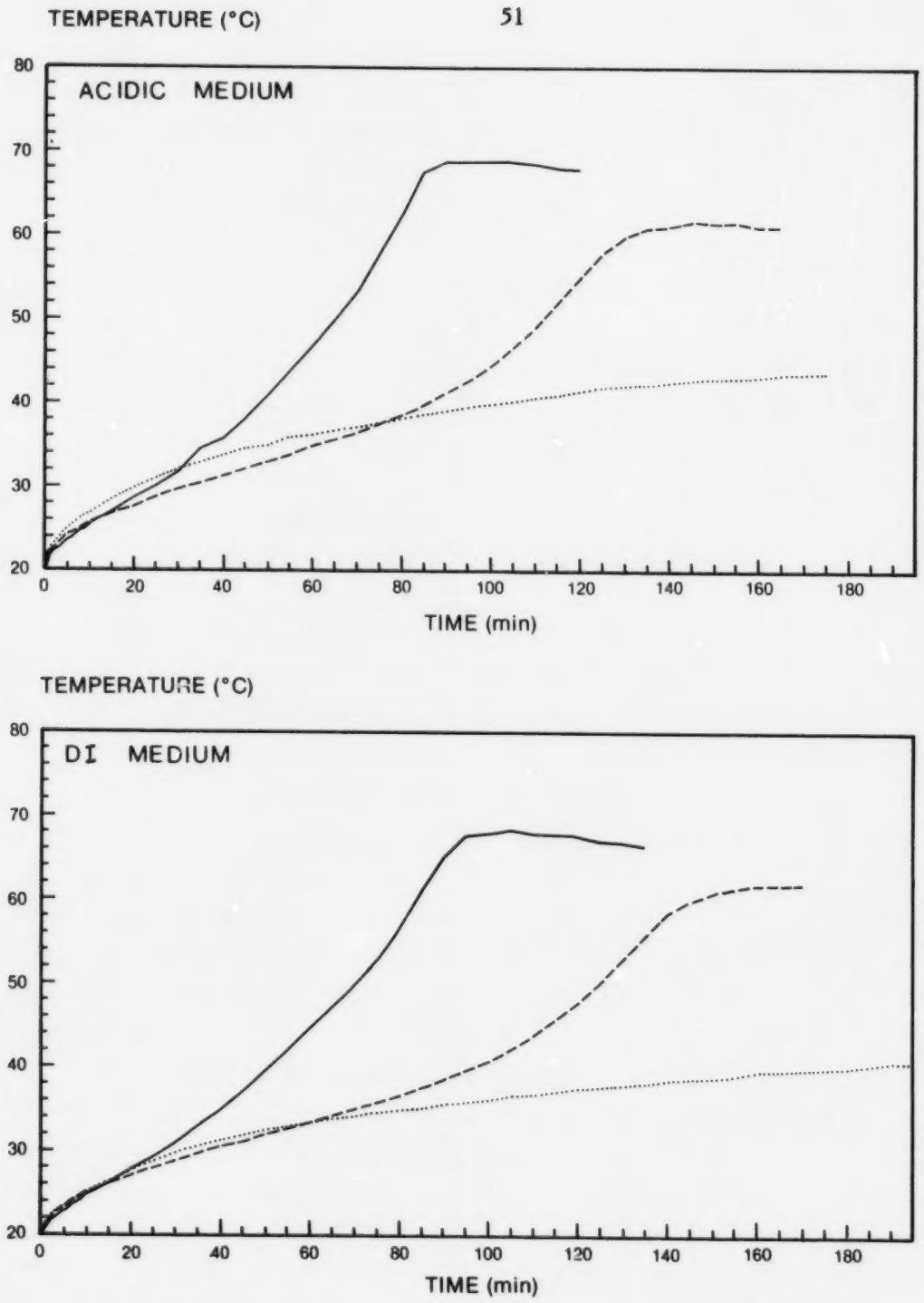


FIGURE 16 TEMPERATURE INCREASES IN THREE DEVCO BED MATERIAL PARTICLE SIZE FRACTIONS AT 1:1 LIQUID TO SOLID RATIOS

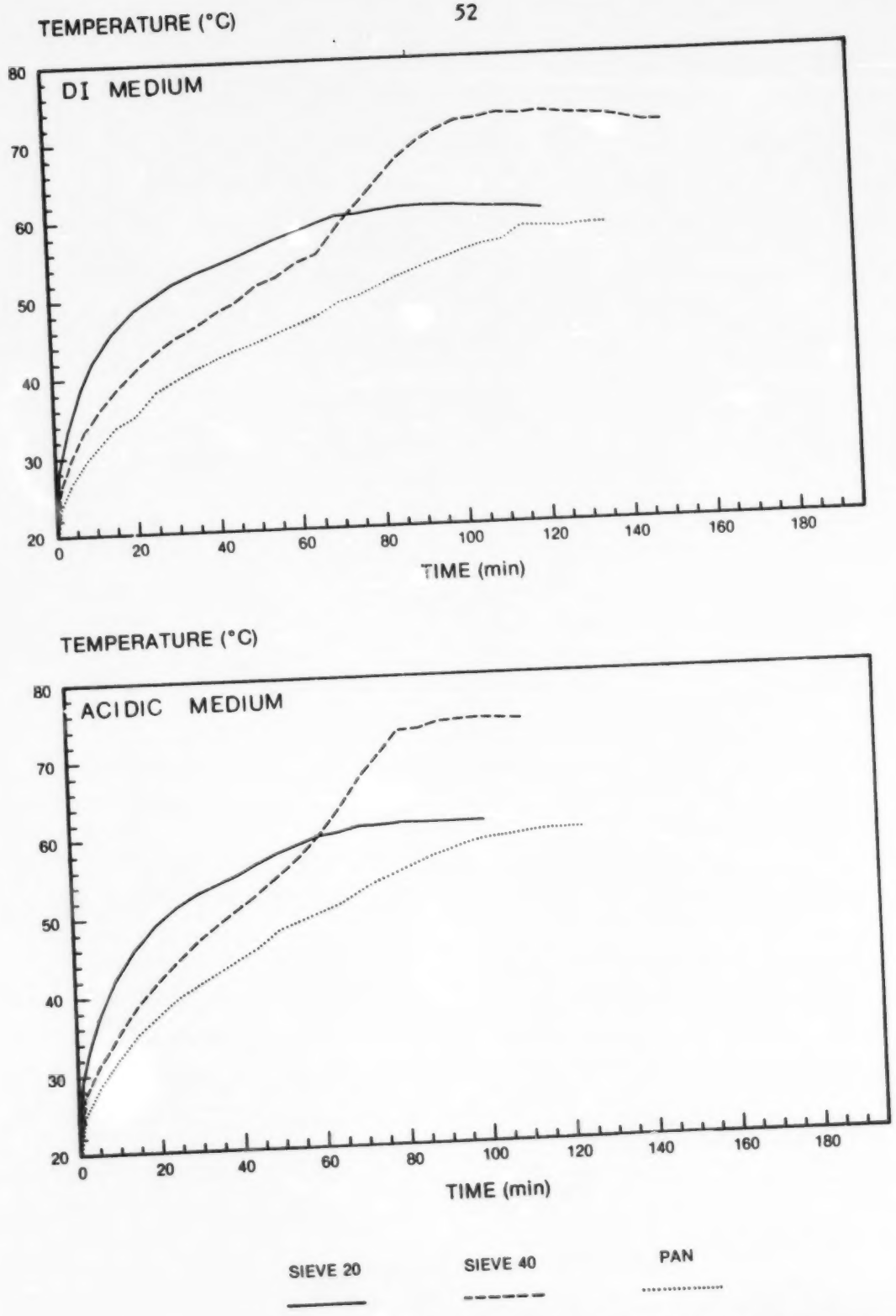


FIGURE 17 TEMPERATURE INCREASES IN THREE MINTO BED MATERIAL PARTICLE SIZE FRACTIONS AT 1:1 LIQUID TO SOLID RATIOS

sieve No. 40 and the pan material. The acidic medium produced a more rapid rate of temperature rise and, in the case of the pan material, a slightly higher temperature increase. Temperature increases during the first 20 minutes were the same for all three Devco bed material fractions.

In the tests on the Minto bed material fractions, for the first 60 minutes the Sieve No. 20 material gave the greatest temperature rise followed by the Sieve No. 40 and pan materials. However, after 60 minutes, the greatest temperature rise was observed in the Sieve No. 40 material. Unlike the Devco bed fractions, differences in temperature increases in the Minto fractions were distinguishable from the start of the tests. The acidic medium produced both a slightly greater temperature rise and rate of temperature rise than did the deionized water.

The amount and rate of heat release may have been influenced not only by the residue contents and liquid-to-solid ratio, but also by particle size since lime slaking theory indicates that the smaller particles should be more reactive. No consistent relationship between particle size and heat release was apparent from the tested bed material fractions in this study. Considerably more study of a greater variety of samples and further development of test procedures would be required to determine the extent of the influence of these variables on the reaction.

4.3.3 Column Exothermic Tests. The exothermic nature of the two bed materials was explored further by filling a column with residue, adding water slowly from the top and monitoring temperature changes at various depths of residue. These tests were conducted to provide some indication of what might occur in a field disposal situation where a layer or pile of dry residue would be exposed to rain. The performance of the test apparatus was also of interest for its ease of use, reproducibility, and possible predictive value.

The first column tests were attempted in a small diameter PVC tube with Minto bed material. PVC pipe was first considered for a test apparatus because it was inexpensive and widely available. After the initial addition of water to this column, a rapid crust formation was observed. This was followed by a violent eruption of material. Some of the erupting material reached the ceiling about two metres above the reaction vessel. In the words of one observer, "It blew up like a bomb". No temperature rise or time recordings were made during this initial test. No further tests were attempted with this size of column.

The second column test, which employed the larger, insulated PVC pipe and dial thermometers, did not produce the initial observable crust formation. Within ten minutes after the initial water addition, though, the material began to swell and overflow the container. Since, at this point the observers retired to a distance too far from the apparatus to reliably record thermometer readings, no temperature data was obtained. Within approximately fifteen minutes, the insulating material began to deform and it was found later that the dial gauges on the apparatus had exceeded their maximum 100°C scale deflection and bent. The PVC pipe itself had deformed and no further tests were attempted with this column.

The third column of stainless steel was then developed (Section 3.4.2). All the column test results provided in this report were generated in this column. Even though the same Minto bed material used in the PVC columns, was subsequently tested several times in this column, the violent reactions and apparent high temperatures achieved in the earlier test were not repeated.

At least two possible reasons for these differences have been advanced. First, the Minto bed material sample may not have been homogeneous even after mixing and the portions of sample used in the two PVC columns coincidentally contained more highly reactive material fractions than were in the rest of the sample. This explanation is not likely since the samples were well mixed before any tests and analyses were initiated. A second hypothesis is that channeling occurred in the column such that water came in contact with dry ash at depth. Due to the insulation of the apparatus and the material itself, the temperature continued to rise until steam was produced. The steam penetrated the dry ash much faster than water could by descent from above. The faster steam penetration, caused the water/ash reaction to accelerate, produce more steam, and force the material above out of the column. As will be shown subsequently, if channeling does not occur then the applied water percolates very slowly through the ash, and only a small amount of ash is wetted at a time as the front progresses. Channeling, however, could permit steam formation and expanding steam could react with a much larger amount of ash in the same time span than a descending water front. The second explanation is more plausible, and indicates not only the problems that could be experienced in a field disposal situation but also the need to include safety precautions for potentially violent reactions in future experiments of this kind. Once again, it must be noted that these results are limited and the possible explanations presented here, are still only hypotheses.

The results of the exothermic tests conducted in the stainless steel column are presented in Figures 18 and 19. Shown are the temperatures at each of the 5

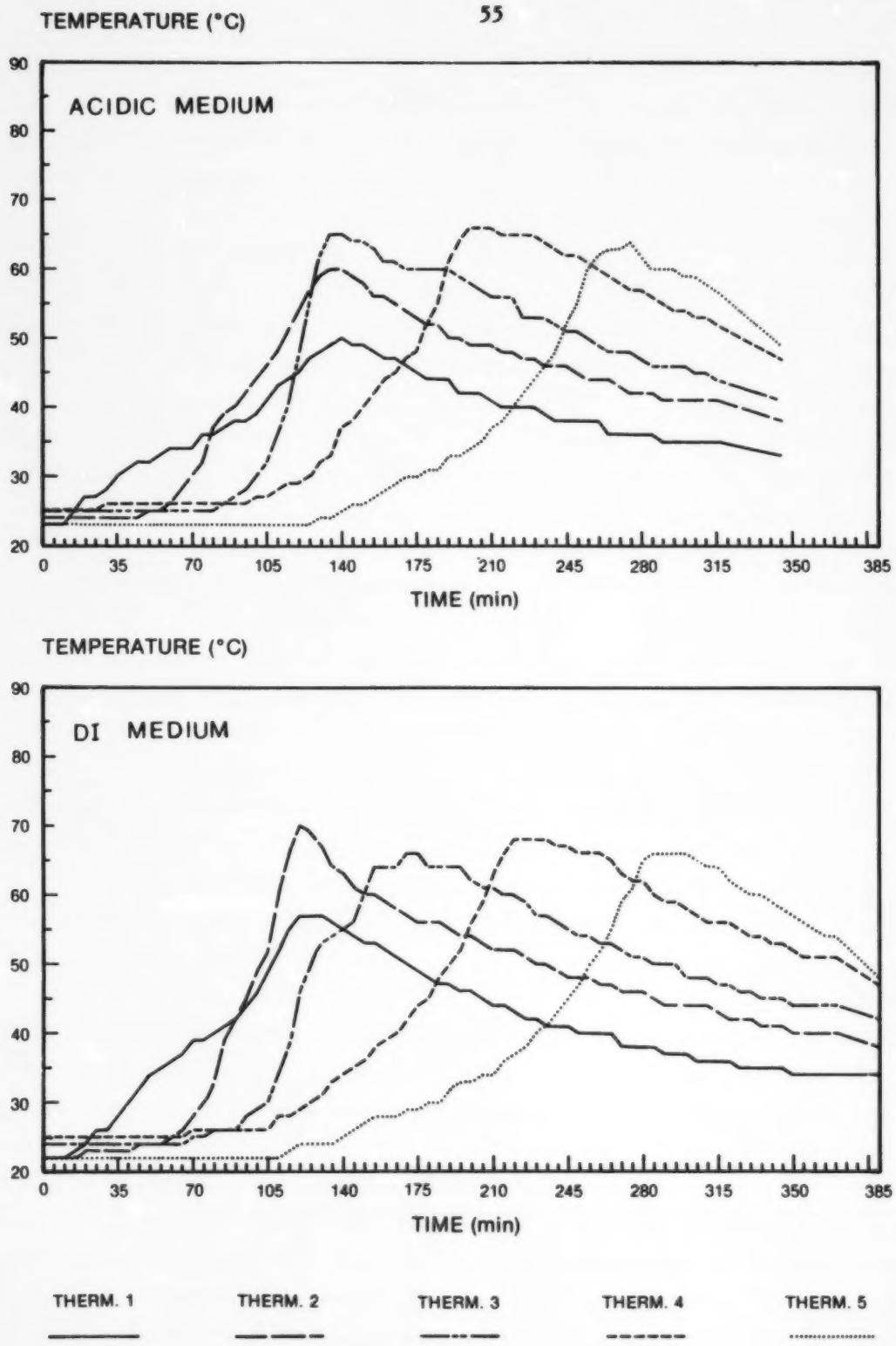


FIGURE 18 TEMPERATURE INCREASE SEQUENCE AT 4 cm INTERVALS IN COLUMN TESTS FOR MINTO BED MATERIAL

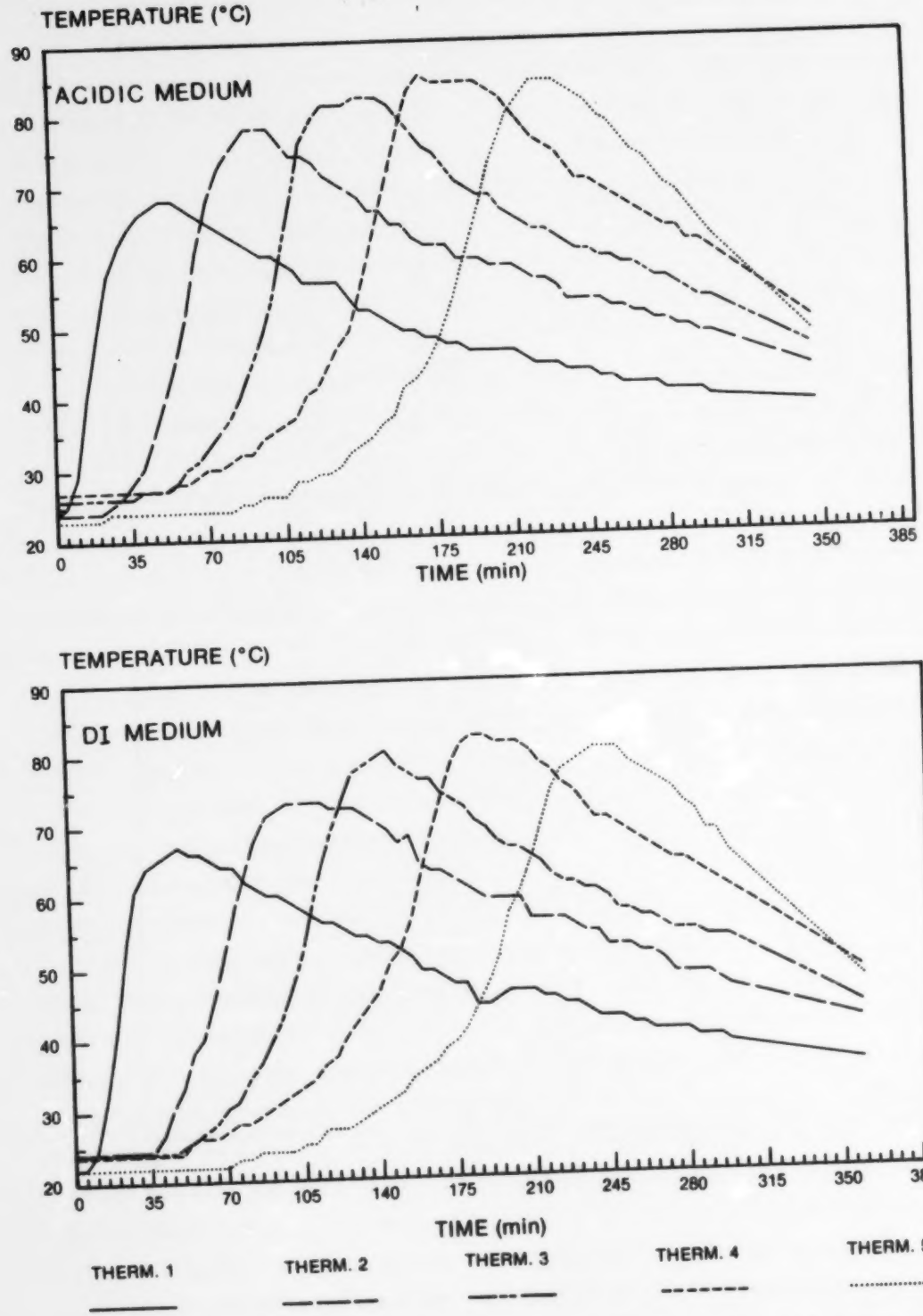


FIGURE 19 TEMPERATURE INCREASE SEQUENCE AT 4 cm INTERVALS IN COLUMN TESTS FOR DEVCO BED MATERIAL

thermometers during application of deionized water and the acidic medium to the top of the column at a rate of 1.24 mL/min. The thermometers were located at 4 cm intervals throughout the residue, with Thermometer No. 1 closest to the top.

The maximum temperature at each thermometer was reached sequentially from the top to the bottom of the column at approximately 50 minute intervals. This indicates that the liquids moved through the column at a relatively uniform rate of approximately 1.3×10^{-3} cm/s. This value is an order of magnitude less than the permeability coefficient of 2.4×10^{-2} cm/s determined using the falling head permeability tests (Section 4.1). However, the permeability tests were conducted with slaked material whereas the materials in the exothermic column were unslaked prior to water application. During these column tests, it was observed that the residues expanded about 10% when wetted. This is consistent with the particle expansion phenomenon described by lime slaking theory. Thus the decrease in permeability may be due to expansion of the slaking CaO in the column into spaces between larger waste particles.

The rates of temperature increase were generally greater near the top of the column. The highest temperatures were reached near the middle of the column. This was as expected due to the insulation provided by the surrounding ash and the walls of the column and because the top and bottom of the column were open to the atmosphere.

For the Minto bed material, a slightly higher and more rapid temperature rise occurred using the acidic medium. In general, the overall shapes of the temperature-time plots for each thermometer, regardless of position or liquid added, were quite similar.

The results for the Devco bed material were less consistent. When deionized water was used, the peak temperatures at Thermometers 1 and 2 occurred simultaneously at an elapsed time of 115 minutes, and the highest and most rapid temperature rise occurred at the second thermometer. When the acidic medium was used, however, the peak temperatures at Thermometers 1, 2 and 3 occurred simultaneously at an elapsed time of 140 minutes even though there were different initial time lags. The highest temperature was recorded at Thermometer 4. In general, temperature peaks were slightly lower with the acidic medium than with deionized water. It appears, therefore, that the chemical composition of the medium affected the reaction.

The maximum temperature increases observed in the column exothermic tests agreed quite favorably with those measured in the extended calorimeter tests if the differences between liquid-to-solid ratios are taken into account. The average liquid-to-solid ratio during the column tests was approximately 0.1:1. The average temperature increases in the Devco and Minto bed materials during these tests were about 45°C and

55°C, respectively, which are about 10 degrees higher than the maximums reached during the extended calorimeter tests at the 1:1 liquid-to-solid ratio.

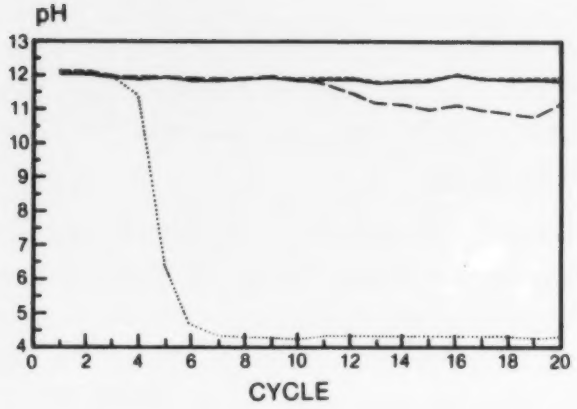
Since no further unstable reactions and no apparatus damage occurred after the steel column was adopted, this apparatus appears to be satisfactory for further column testing. However, considerably more experience with this apparatus is still needed to provide a better basis for its evaluation. The results suggest that higher temperatures are possible with larger insulated masses of material. Factors that affect water contact rate also appear to be important.

4.4 Leaching Properties

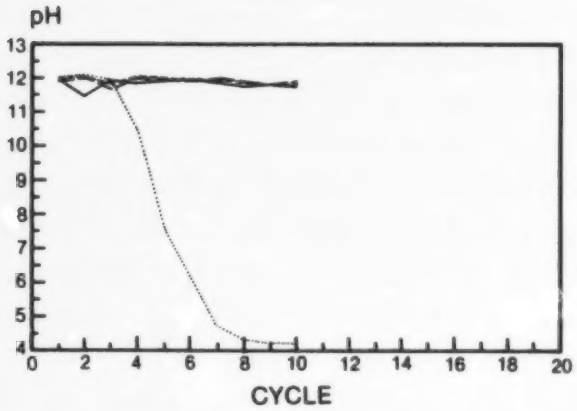
Serial batch leaching tests were used to examine the solubility of the residues in distilled water and an acidic leaching medium at 4:1 and 20:1 liquid-to-solid ratios. On a hydraulic loading basis, each leaching cycle conducted at the 20:1 ratio is equivalent to five cycles conducted at the 4:1 ratio. The Devco bed material was leached for 10 cycles whereas the Minto bed and Devco baghouse materials were leached for 20 cycles. Conductivity, pH and TDS concentrations were measured in the leachates after every cycle. The results of these analyses are given in Tables A.1 to A.3 in the Appendix. Chemical anlayses were conducted on the Devco bed leachates from Cycles 1, 4 and 10, and on the Minto bed and Devco baghouse leachates from Cycles 1, 2, 4, 6, 10, 15 and 20. The solids remaining at the end of the tests were chemically analyzed. Results of these leachate and solid analyses are presented in the Appendix.

4.4.1 Leachate pH. Variations in leachate pH during the 10 or 20 cycles are plotted in Figure 20. Leachate pH's for both bed materials remained relatively constant throughout the tests at about 12 except for the 20:1 acidic medium leachates, where pH dropped rapidly after 3 cycles. Leachate pH's for the Devco baghouse material varied considerably depending on the leaching medium and the liquid-to-solid ratio. Distilled water leachate pH's decreased only slightly during the 20 cycles from about 11.0 to 10.3, whereas acidic medium leachate pH's decreased rapidly after the first cycle and reached the pH of the leaching medium (4.5) after about 19 cycles at the 4:1 ratio and about 5 cycles at the 20:1 ratio. On a hydraulic loading basis, the pH of the acidic medium was achieved in the leachates from both tests after a cumulative liquid-to-solid ratio of about 80:1 had been reached.

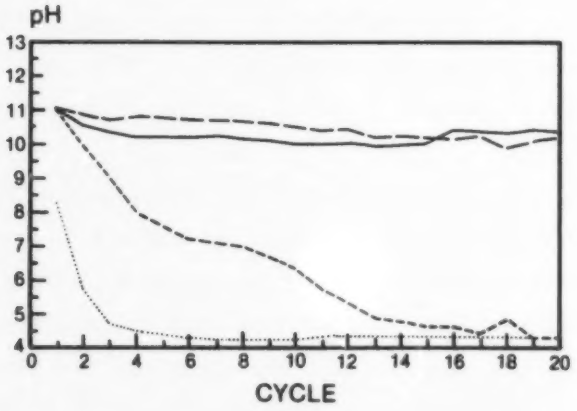
The high pH values of the distilled water leachates and the initial acidic medium leachates indicated they would be toxic in the environment. The decline of bed waste leachate pH only after a cumulative liquid-to-solid ratio of about 80:1 had been



Minto Bed



Devco Bed



Devco Bag

DI MEDIUM 4:1 — DI MEDIUM 20:1 — ACIDIC MED. 4:1 — ACIDIC MED. 20:1

FIGURE 20 pH VERSUS SERIAL BATCH LEACHING CYCLE

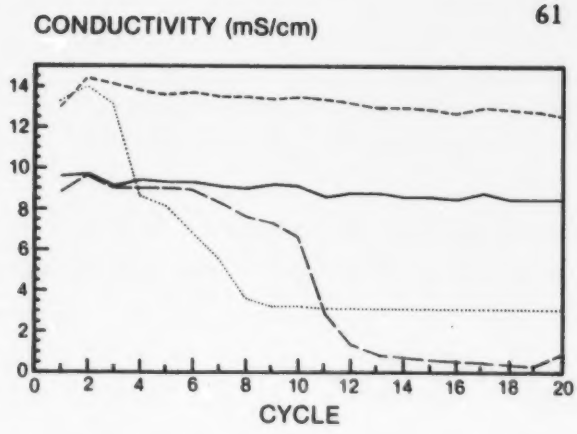
reached with the acidic medium confirmed the presence of substantial soluble alkaline material as indicated in the acid neutralization and CaO content determinations. The results suggest that continued alkaline leaching would occur for a long time in disposal situations where repeated water contact was permitted.

4.4.2 Conductivity. Variations in leachate conductivities are plotted in Figure 21. Electrical conductance is often proportional to the concentration of dissolved ionic species in an aqueous solution, and a conductivity measurement can provide a quick and simple way to determine residue leachability (i.e., if ions can be released from the solid into an aqueous medium). However, it does not reveal the types of ions in solution.

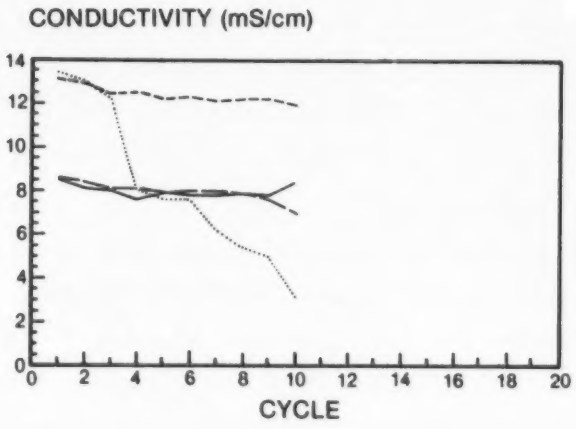
The conductivities of the bed material leachates at the 4:1 liquid-to-solid ratio decreased slightly during the tests to reach approximately 12 mS/cm in the acidic medium leachates and 8.5 mS/cm in the distilled water leachates. At the 20:1 liquid-to-solid ratio, the conductivities of the distilled water leachates remained fairly constant at about 8 to 9 mS/cm up to Cycle 6, then decreased to 7 mS/cm at Cycle 10 for the Devco bed material and to less than 1 mS/cm after Cycle 12 for the Minto bed material. The conductivities of the acidic medium leachates at the 20:1 ratio decreased rapidly after the first three cycles from about 13 to 3.1 mS/cm at Cycle 10. It is apparent that the acidic medium did increase the rate of ion release into solution, however it must be noted that the conductivity of the acidic leaching medium by itself is about 3.1 mS/cm.

The conductivities of the distilled water leachates from contact with the Devco baghouse material decreased from about 5 mS/cm at Cycle 1 to less than 1 mS/cm after Cycle 14 with the 4:1 ratio and after Cycle 3 with the 20:1 ratio. The conductivities of the acidic medium leachates were much higher, and decreased from 10 to 13 mS/cm at Cycle 1 to 5.5 mS/cm at Cycle 20 with the 4:1 ratio and to the conductivity of the acidic medium after Cycle 7 with the 20:1 ratio.

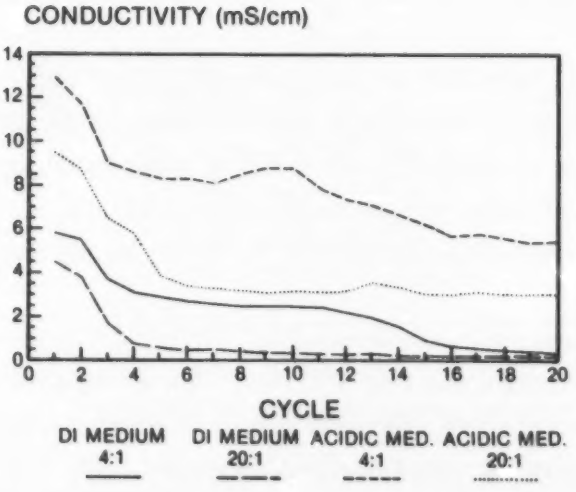
Generalizing these results on the basis of cumulative liquid-to-solid ratios, the bed materials continued to release ions into solution until an amount of leaching medium approximately equal to 200 times the mass of leached solid had been contacted with the wastes, whereas the baghouse material released ions into solution until a cumulative liquid-to-solid ratio of 100:1 (i.e., one-half the ratio for the bed materials) had been achieved. At equivalent cumulative liquid-to-solid ratios, the conductivities of the acidic medium leachates were generally higher than those of the distilled water leachates. Part of these higher conductivities was due to the conductivity of the acidic medium itself (approximately 3.1 mS/cm).



Minto Bed



Devco Bed



Devco Bag

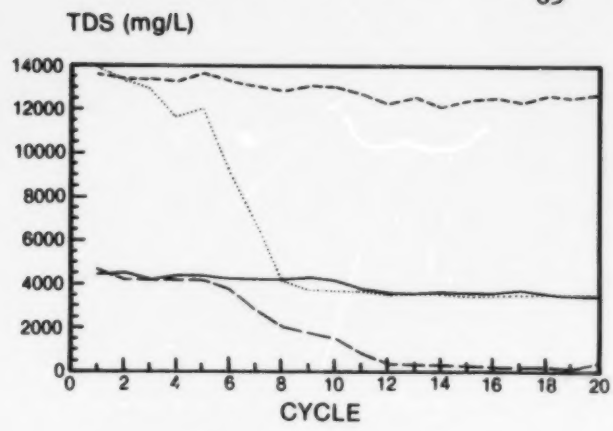
FIGURE 21 CONDUCTIVITY VERSUS SERIAL BATCH LEACHING CYCLE

4.4.3 Total Dissolved Solids. Variations in total dissolved solids (TDS) concentrations in the leachates are plotted in Figure 22. They generally followed the same trends displayed by leachate conductivities. TDS concentrations in the bed material leachates at the 4:1 liquid-to-solid ratio remained relatively constant throughout the tests at about 13 000 mg/L in the acidic medium leachates and about 4000 mg/L in the distilled water leachates. At the 20:1 ratio, however, they decreased rapidly after the sixth leaching cycle. In the acidic medium leachates they decreased from about 14 000 to 4000 mg/L (the TDS concentration of the acidic medium itself) whereas in the distilled water leachates they decreased from 4000 to 2000 mg/L over 10 cycles of the Devco bed material and from 4000 to about 200 mg/L over 20 cycles of the Minto bed material. TDS concentrations in the Devco baghouse leachates decreased steadily throughout the tests at the 4:1 ratio, and decreased rapidly during the first 4 to 6 cycles at the 20:1 ratio then levelled off at about 4000 mg/L in the acidic medium leachates and about 200 mg/L in the distilled water leachates. These TDS levels are much higher than those normally encountered in natural surface waters.

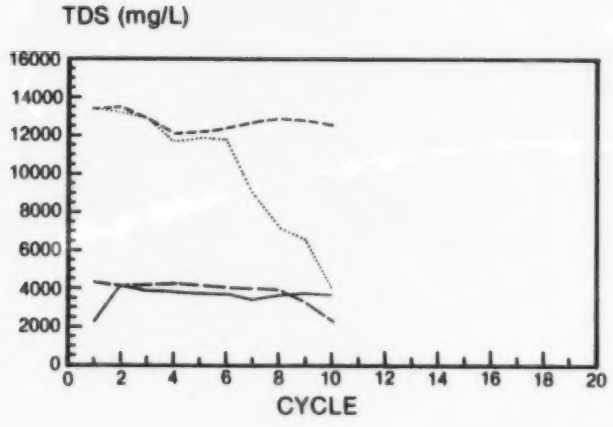
4.4.4 Leachate Chemical Composition. Variations in the concentrations of selected ions in the leachates from the three residues at the 20:1 liquid-to-solid ratio are shown in Figures 23 and 24. The constituents selected for illustration are sulphate, sodium, magnesium, iron and calcium. Sulphate and calcium were selected since they are major constituents of AFBC residues. Sodium is a highly soluble metal which is easily leached and is often a major constituent of total dissolved solids. The solubilities of magnesium and iron are largely controlled by pH and redox; therefore, their behaviour in solution can be used as a first approximation for many other metals of concern.

In general, the highest concentrations observed were for calcium and sulphate ions in the distilled water leachates, and sodium, calcium and sulphate ions in the acidic medium leachates. These concentrations were usually 3 to 4 orders of magnitude larger than the concentrations of the other selected elements. The sodium concentrations in the acidic medium leachates, however, were largely or perhaps wholly due to the large sodium content of the acidic medium itself.

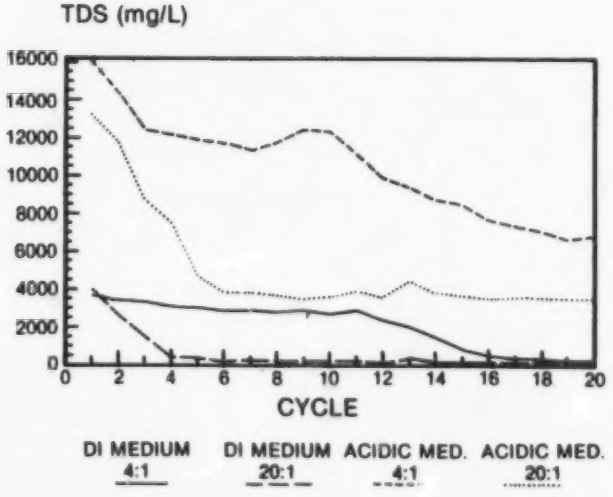
In the distilled water leachates, concentrations either remained relatively constant or decreased by up to an order of magnitude over the 10 or 20 leaching cycles. In the acidic medium leachates, some concentrations decreased over time whereas others increased. For example, calcium and sulphur ion concentrations decreased from 1 to 2 orders of magnitude whereas magnesium and iron concentrations increased by 2 to 3



Minto Bed

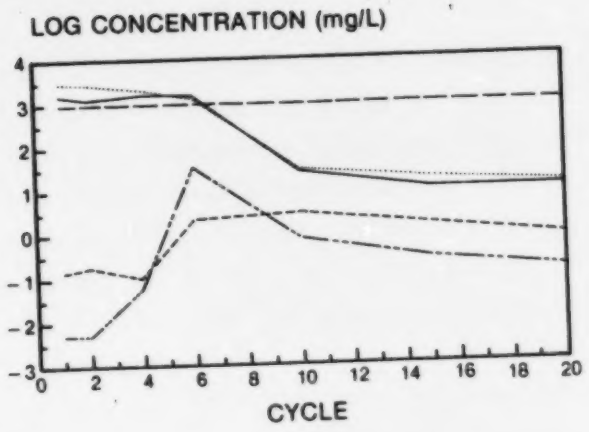


Devco Bed



Devco Bag

FIGURE 22 TDS VERSUS SERIAL BATCH LEACHING CYCLE



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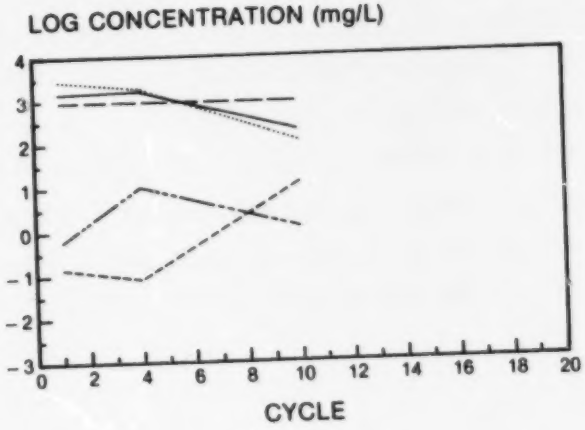
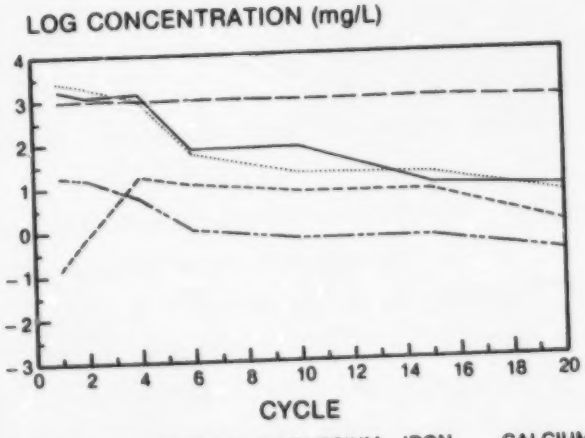
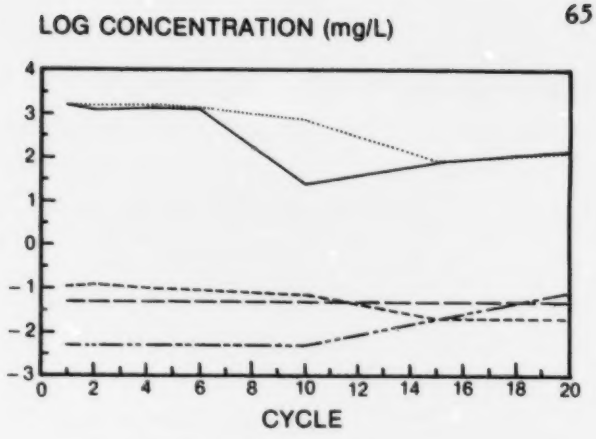


Devco Bed

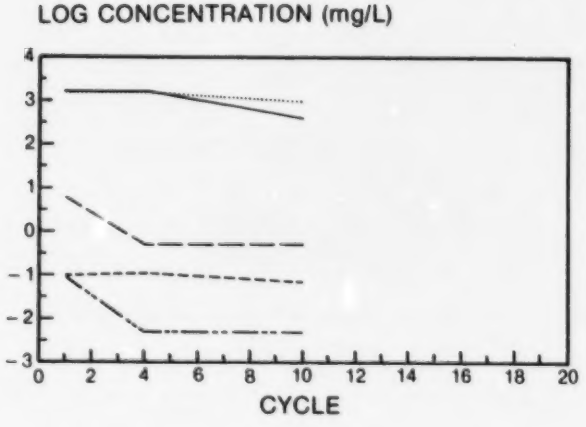


Devco Bag

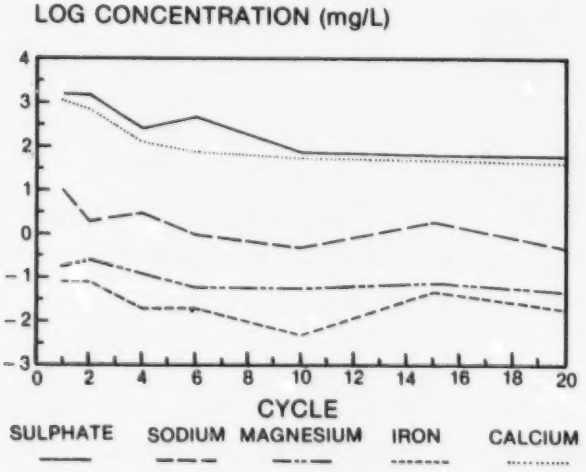
FIGURE 23 IONIC CONCENTRATIONS VERSUS ACIDIC MEDIUM SERIAL BATCH LEACHING CYCLES



Minto Bed



Devco Bed



Devco Bag

FIGURE 24 IONIC CONCENTRATIONS VERSUS DI MEDIUM, SERIAL BATCH LEACHING CYCLES

orders of magnitude. The commencement of the increases in the magnesium and iron concentrations and the decreases in the calcium and sulphate concentrations generally coincided with a decrease in leachate pH. Concentrations in the distilled water leachates remained relatively constant because leachate pH remained high throughout the leaching tests.

The results of these serial batch leaching tests indicate the potential for continued high rates of leaching from these wastes, and the significant changes that can occur in the chemical composition of the leachates with time. They also show that only one batch leaching test of a material of this kind would not reveal the later changes in leachate composition, such as the substantial increases in the magnesium and iron concentrations in the acidic medium leachates.

4.4.5 Composition and Weight Loss of Leached Solids. The solids remaining at the end of each leaching test were subjected to elemental and X-ray diffraction analyses to determine their elemental and crystalline composition. The results of these analyses are presented in the Appendix.

The amount of residue dissolved during the 10 or 20 leaching cycles was determined by weighing each residue before and after a leach test. The calculated weight losses are given in Table 16 and the Appendix. The highest weight losses were observed for the acidic medium at the 20:1 liquid-to-solid ratio. The weight losses under these conditions were 83% for the Devco bed material (the highest even though it was only subjected to 10 leaching cycles), 64% for the Minto bed material and 32% for the Devco baghouse material. These calculations should only be used as an indication of the relatively high solubility of these materials because they do not take into account losses that might have occurred by other means (e.g., solids retention on filter papers).

4.4.6 Leachates from the Column Exothermic Tests. Samples of leachate were collected during the column exothermic tests and analyzed for pH, conductivity, total solids and total dissolved solids. The leachates were highly alkaline with high total dissolved solids concentrations. The results in the Appendix compare very favorably with those from the serial batch leaching tests, as shown in Table 17.

4.5 Quality Control

The comparative analysis of the standard PFC ash reference material as certified by the U.S. National Bureau of Standards and the results of the analyses by the methods used during this study are presented in Table 18. The results reported as

TABLE 16 PERCENT WEIGHT LOSS DURING LEACHING TESTS*

Material	Leaching Conditions			
	Distilled Water		Acidic Medium	
	4:1	20:1	4:1	20:1
Minto Bed	11	54	30	64
Devco Bed	0.6	66	4.5	83
Devco Baghouse	9.6	19	15	32

* during 10 cycles for the Devco bed material and 20 cycles for the other materials

TABLE 17 COMPARISON OF LEACHATES FROM COLUMN EXOTHERMIC TESTS AND BATCH LEACHING TESTS

Material	Leaching Medium	pH		Conductivity (mS/cm)		TDS (mg/L)	
		Column	Batch*	Column	Batch*	Column	Batch*
Minto Bed	D. Water	12.4	11.8 to 12.1	8.0	8.5 to 9.7	5 130	3 500 to 4 490
	Acidic	12.3	11.8 to 12.1	12.4	12.6 to 14.4	15 800	12 100 to 13 600
Devco Bed	D. Water	12.3	11.5 to 12.0	7.9	7.6 to 8.5	5 070	2 210 to 4 110
	Acidic	12.3	11.8 to 12.1	12.0	12.0 to 13.1	17 000	12 100 to 13 500

* range observed over 20 (Minto) or 10 (Devco) leaching cycles at 4:1 liquid-to-solid ratio

measured values are from inductively coupled argon plasma spectroscopy, atomic absorption spectroscopy and neutron activation analyses.

The measured values agree favorably with the certified concentrations with the exceptions of barium, chromium, cobalt, lead, manganese, nickel and strontium, which were underestimated by 13 to 35%, and of sodium and mercury which were overestimated by 24 and 38%.

Results of the quality control program on the spiked leachate samples are given in Table 19. In general, recoveries ranged between 85 and 95%, indicating that the

TABLE 18 COMPARATIVE ANALYSIS OF A STANDARD REFERENCE MATERIAL

Parameter	Certified Values*	Measured Values	Percent Recovery
Aluminum (%)	14.0	13.4	95.7
Arsenic	145 ± 15	132	91.0
Barium	1500	1300	86.7
Beryllium	12.0	11.6	96.7
Cadmium	1.0 ± 0.15	< 1	99.9
Calcium (%)	1.11 ± 0.01	1.09	98.2
Chromium	196 ± 6	161	82.1
Cobalt	46	37	80.4
Copper	118 ± 3	117	99.2
Iron (%)	9.4 ± 0.1	9.2	97.9
Lead	72.4 ± 0.4	60.0	82.9
Magnesium	4550 ± 100	4050	89.0
Manganese	190	164	86.3
Mercury	0.16 ± 0.01	0.22	138
Nickel	127 ± 4	105	82.7
Potassium (%)	1.88 ± 0.06	1.90	101
Silicon (%)	22.8 ± 0.8	22.2	97.4
Sodium	1700 ± 100	2100	124
Strontium	830 ± 30	542	65.3
Thorium	24.7 ± 0.3	22	89.1
Titanium	8000	7860	98.3
Uranium	10.2 ± 0.1	11	108
Vanadium	300	281	93.7
Zinc	220 ± 10	211	95.9

Note: all results expressed as µg/g unless otherwise stated
* standard Reference Material 1633a (Coal Fly Ash) from the National Bureau of Standards

analytical techniques tended to slightly underestimate leachate concentrations. The lowest recoveries of 80 and 77% were observed for cadmium; however, the concentrations in the samples were very close to the detection limit.

TABLE 19 QUALITY ASSURANCE TESTING FOR AFBC LEACHATE SAMPLES

Parameter	Detection Limits	Sample Description	Initial Value (mg/L)	Spike Added (mg/L)	Measured Value (mg/L)	Expected Value (mg/L)	Percent Recovery
Aluminum	<0.01	BH-20D-4	1.02	2.5	3.45	3.52	98.0
		BH-20A-10	22.1	18.5	37.3	40.6	91.9
Calcium	<0.01	MB-20A-10	28.1	47.5	62.5	75.6	82.7
		MEDIA A	< 0.1	325	295	325	90.8
Cadmium	<0.01	BH-4A-1	0.05	0.05	0.08	0.10	80.0
		MB-20D-4	0.03	0.10	0.10	0.13	76.9
Copper	<0.008	BH-20A-10	0.093	0.093	0.187	0.186	100.5
		MB-20A-1	0.010	0.500	0.460	0.510	90.2
Chromium	<0.01	BH-20D-1	0.09	0.10	0.23	0.19	121
		BH-4D-1	0.23	0.50	0.69	0.73	94.5
Iron	<0.01	MB-20A-10	2.89	0.50	3.26	3.39	96.2
		BH-20A-10	7.31	9.30	15.30	16.61	92.1
Nickel	<0.05	BH-4A-1	0.18	0.10	0.31	0.28	110.7
		MB-4D-10	0.12	1.0	0.95	1.12	84.8
Magnesium	<0.01	DB-20A-10	1.19	2.0	2.74	3.19	85.9
		BH-4A-4	10.4	15.0	23.4	25.4	92.1
Manganese	<0.01	DB-20A-10	0.43	0.30	0.70	0.73	95.9
		BH-20A-4	0.70	3.00	3.24	3.70	87.6
Potassium	<1	BH-4D-10	5	5	11	10	110
		BH-20D-1	27	40	67	67	100
Sodium	<1	DB-20D-1	6	20	25	26	96.2
		MEDIA D	< 1	200	179	200	89.5
Silicon	<0.05	BH-20D-10	3.00	2.50	5.60	5.50	101.8
		BH-20A-10	30.8	20.0	50.7	50.8	99.9
Zinc	<0.01	DB-4A-10	0.18	0.10	0.25	0.28	89.3
		BH-20A-4	0.50	1.00	1.30	1.50	86.7

Note: all results expressed in mg/L unless stated otherwise
BH - DEVCO BAGHOUSE
DB - DEVCO BED
MB - MINTO BED

Example: BH - 20D - 10 ← Cycle Number

BH: Devco Baghouse

20D: Liquid to solid ratio (20:1); Leaching Media used (Distilled Water)

4.6 Evaluation of Residue Characterization Methods

The standard elemental analysis techniques which are commonly employed for PCF ashes and leachates appear to be suitable for these AFBC wastes. Unlike PCF solid analyses, the actual amounts of crystalline calcium oxide and perhaps other major calcium salts in the solids appear to be important, particularly with respect to the exothermic nature of these residues. Unfortunately, no simple and inexpensive method is available as yet for quantifying these calcium compounds. Hopefully simple surrogates can be found which will act as acceptable substitutes for these determinations.

The procedures used to measure the physical properties of the residues appear to be adequate, except for the hydrometer method used for the determination of particle sizes below 200 mesh. This method is not appropriate for soluble materials of this type. The effects of waste reactions with water should be considered in measurements in which water is involved.

The exothermic properties of the residues were examined using calorimeter and column tests. The calorimeter test is similar to that given in ASTM C110-76a for determining the slaking rate of calcined limestone. It appears to be suitable as a simple and rapid method for comparing heat release from different AFBC residues under identical test conditions, but not for predicting problems that might occur because of the exothermic nature of these residues. For example, it did not indicate the potential for the rapid and violent reactions which were encountered in the initial column tests. This method is not suitable at low liquid-to-solid ratios since a viscous paste is formed which is difficult to mix, or when large solid particles are present because they may shatter the fragile liner of the Dewar flask.

The column exothermic test procedure went through several modifications during the study. A test of this type appears to be more suitable than the ASTM method for evaluating the potential problems that might occur during handling and disposal, and for exploring heat release patterns under different experimental conditions. However at this stage of development it is more time and labor intensive and the possibility of further violent reactions has not been eliminated.

The leachability of each residue was evaluated using a serial batch leaching test. An extended leaching test of this type should be used on these wastes rather than a single batch test because of the high solubility of the wastes and the changes that occur in the chemical characteristics of the leachates with time. TDS, conductivity and pH measurements on the leachates provided useful information on these chemical changes,

and were relatively simple to perform. They could be used in future leaching tests and in field leachate monitoring studies as surrogate parameters to flag changes in leachate composition and to indicate when more detailed chemical analyses should be performed.

5 SUMMARY AND RECOMMENDATIONS

5.1 Summary

Atmospheric fluidized bed combustion technology is being developed as a means for combusting variable quality solid fuels and for controlling sulphur and nitrogen emissions during combustion. Although the major emphasis to date has been placed on improving the design an operation of this technology, there has also been a growing awareness of the potential problems and local environmental consequences of handling and disposing of AFBC solid wastes.

No full-scale AFBC units existed in Canada from which combustion residues could be obtained for testing and analysis. However, three solid waste samples of bed and baghouse materials were available from a U.S. AFBC test facility which had conducted tests of eastern Canadian high sulphur content coals in a bed of Canadian limestone. These samples were used in this study to provide a preliminary evaluation of the characteristics and potential environmental problems of AFBC solid residues.

The study included a critical literature review to summarize the properties of the AFBC wastes reported in the literature, identify those properties that appeared to be significant from an environmental protection perspective, and identify testing procedures that could be used for laboratory examination of these properties. The physical, chemical, exothermic and leaching properties of the three AFBC combustion waste samples were evaluated using these and other procedures.

The literature review indicated that the characteristics of some AFBC solid wastes had been examined, in varying degrees, in both the United States and Europe. Generalizations and direct comparisons of results from these studies were often difficult due to the lack of description of combustion conditions and test procedures, differences among test procedures, and inconsistent use of conventions for reporting test results. It appeared that no standard protocol or battery of test procedures was available for characterizing the properties of AFBC solid wastes.

The literature indicated that the wastes were highly alkaline, well buffered, and composed primarily of calicum, sulphate, silica, and iron. Limitations in the manner of reporting made it difficult to determine the major crystalline species which might be present. Relatively low metal concentrations, similar to other coal combustion residues, were reported. No detailed information on the organic constituent of the wastes was available.

Reported leaching properties consistently indicated high pH, and high TDS, sulphate and calcium concentrations. Trace element concentrations in leachates appeared to be low.

There were several reports of heat release from solid waste/water reactions, although some of the results appeared to be contradictory. The major cause for the exothermicity of these wastes was reported to be the presence of unslaked calcium oxide; however, the factors which controlled these reactions did not appear to be clearly understood.

As a result of the critical literature review, batteries of tests for waste and leachate characterizations were selected. In some cases the procedures were significantly modified during the course of the study in order to explore certain characteristics more thoroughly.

Standard test procedures were used to determine the following physical properties of the residues: moisture content, specific gravity, water holding capacity, permeability, particle size distribution and moisture/density relationships. Bed materials were composed of coarse, poorly graded, sand-sized particles. The baghouse material was composed of more uniform, finer particles. Hydrometer analyses for small particle size fractions were attempted but gave unreliable results because the residues were highly soluble and appeared to react with the chemical additives used in the analyses. Thus this procedure is not appropriate for fine particle sizing of AFBC residues of the type examined in this study.

Both bed material samples contained little or no moisture, but the baghouse sample had a moisture content of 5.4%. The specific gravities of the three residues were approximately the same, and ranged between 2.80 and 2.93 g/cm^3. The baghouse material retained two to three times as much water against the force of gravity as the bed samples and its permeability coefficient was two to three orders of magnitude lower. The bed material permeabilities approximated those of medium sands while the baghouse permeability was significantly less. In general, these test results compared favourably with those reported in the literature. In subsequent column tests, however, the permeabilities of the bed materials were estimated to be an order of magnitude less than those indicated in these tests. This decrease was probably due to expansion of the ash in the column and the subsequent reduction in the void spaces between the particles. This expansion did not occur during the permeability tests because the materials were hydrated prior to placement in the permeameter.

The pH values of the materials ranged from 10.8 for the baghouse sample to 12.2 for the bed material samples. The acid neutralization capacity of both bed materials was 9 gram-equivalents of 1 N H_2SO_4 per kilogram of residue, whereas that of the baghouse material was only 2.7.

Since little documented information was available on the chemical composition of AFBC residues, and because no optimum methods for their chemical characterization appeared to have been developed, a comprehensive analytical program involving ICAP, AA, NAA, XRD, and XRF analyses was followed. In addition, a detailed quality control program was followed to ensure that the analytical methods used gave acceptable results. The results of this program and the confirmatory data provided by the various analytical methods indicated that precise reproducible results for elements could be achieved for AFBC materials using the standard digestion and analysis techniques used for pulverized coal ash.

The residues contained major amounts of calcium, silicon, sulphur, aluminum, and iron as well as a wide variety of trace elements. The minor elements in the residues were similar to those in other coal combustion residues; however, a significant difference was that the bed materials contained large portions of their calcium in the reactive crystalline calcium oxide form rather than in a glassy calcium aluminosilicate matrix. The quantitative estimation of crystalline and other chemical species is non-standard.

The radiochemical characteristics of the wastes were determined with alpha and gamma spectroscopy. The activities of the natural radionuclides were relatively low and comparable with those found in other coal combustion wastes.

Exothermic properties of the bed materials were examined in detail and efforts were made to develop simple reproducible tests to facilitate this type of examination in future. Heats of reaction were determined in a calorimeter, and averaged 124 kJ/kg in the Minto bed material, 38 kJ/kg in the Devco bed material, and only 14 kJ/kg in the Devco baghouse material. These values may underestimate the exothermicity of fresh residues since the samples were in uncertain storage for several years prior to these tests and the baghouse material had a moisture content of 5.4% when received.

The exothermic nature of the residues was examined further by filling a column with residue, adding water slowly from the top, and monitoring temperature changes at various depths of residue as the water descended. This column exothermic test was developed to more closely approximate field conditions where a layer or pile of dry residue would be exposed to rain. Several modifications had to be made to the test procedure and apparatus during the study because of the violent reactions and high

temperatures that were achieved in some of the initial tests. All of the factors which may contribute to these unusually fast reactions were not clearly identified in this study. However, in addition to crystaline CaO, the reactions may be caused by some combination of conditions such as chemical and/or physical waste characteristics, column packing, column geometry, and/or water addition rates. The practical upper limits of these reactions and the probability of their occurrence in field situations should be examined in future studies.

In the less violent reactions using a steel column, average temperature increases of about 45°C and 55°C were observed in the Devco and Minto bed materials, respectively. The rates of temperature increase were generally greater near the top of the column. The highest temperatures were reached near the middle of the column. This was as expected because of the insulation provided by the surrounding ash and the walls of the column, and because the top and bottom of the column were open to the atmosphere.

The leaching properties of the residues were evaluated using serial batch leaching tests. The wastes were leached for 10 or 20 cycles with distilled water and an acidic leaching medium at 4:1 and 20:1 liquid-to-solid ratios. The residues were found to be readily soluble in both media, and generated leachates that were highly alkaline with high calcium and sulphate concentrations. The bed materials continued to release ions into solution until an amount of leaching medium approximately equal to 200 times the initial mass of the leached solid had been contacted with the wastes. The comparative value for the baghouse material was 100. This behaviour differs significantly from that of pulverized coal-fired ashes which are generally much less soluble.

The tested AFBC residues were found to possess unique properties compared to conventional coal combustion wastes. Most notable among these properties were reactivity, high alkalinity, high leachability, and exothermicity. The significance of these properties with respect to waste management and disposal considerations is not yet fully understood. Further studies on fresh samples from other AFBC units need to be conducted to determine if these properties are representative of AFBC wastes in general or even of AFBC wastes generated from the combustion of high sulphur coals in limestone beds.

5.2 Recommendations

In view the paucity of information available concerning AFBC wastes in general and AFBC wastes from eastern Canadian high sulphur coal/limestone mixtures in

particular, including the results of this study, a large number of hypotheses and recommendations for further studies can easily be made:

1. Due to the small number, history, and nature of the samples tested, characterization of a variety of fresh, properly stored AFBC residues is now desirable in order to determine the extent to which the observed properties of the three study samples are shared by other similar AFBC wastes.

2. Theoretical considerations, results in the literature, and observations made during this study all indicate that there is a potential for a rapid thermal reaction to occur under some as yet undefined conditions when some AFBC wastes contact water. Further studies to define these conditions, the potential for their occurrence under full-scale operational conditions, and the significance of these reactions with respect to environmentally safe waste handling and disposal methods, should be initiated.

3. The results suggest that, possibly, the addition of woodchips to the coal feed increased the exothermic property of the spent bed material in some way. The effects of variations in the chemical composition of the fuels and bed materials on waste composition and reactive characteristics require further study to determine if certain waste constituents alter reactivity or other waste characteristics significantly.

4. Since the crystalline calcium oxide content of these wastes appears to be a significant contributor to their reactive properties, the quantitative determination of crystalline CaO and other major crystalline calcium forms as well as the refinement of the methods for their determination, should be continued.

5. The calcium content of combustion wastes is often reported only as the calcium content "... as CaO". Since the actual crystalline calcium oxide content of AFBC wastes appears to be significant, reporting of this nature should be expanded to clearly indicate that such results are not an estimate of the actual crystalline calcium oxide content.

6. The presence of elemental sulphur in these wastes has been suggested. The presence of a quantity of sulphur in this form in fresh samples would indicate that unusal combustion conditions or chemical reactions which have not yet been taken into consideration, may be occurring during AFBC combustion. The determination of the amount of elemental sulphur present in fresh samples, therefore, should be included in future waste characterizations.

7. The potential influence of combustor operating conditions on waste characteristics requires further examination.

8. The organic contents of AFBC wastes may be greater than those of conventional coal-fuelled combustion wastes. The nature and quantities of the organic constituents of these wastes require examination.

9. The toxicity of water contaminated by AFBC wastes should be examined by standard biological assay methods.

10. A study to identify practical treatment methods for AFBC waste contaminated waters should be initiated.

11. The column and calorimeter examinations of the wastewater reactions and heat release patterns should be continued and compared in future characterization studies. If indicated to be beneficial for further heat release pattern characterization, column test apparatus development should also continue. In view of the rapid reactions observed in initial column experiments in this study, safety precautions should be taken.

12. The operation of the column apparatus in a water upflow mode would appear to eliminate the potential for unpredictable effects from water channelling. However, in view of the as yet undefined reaction conditions and limits and potential hazard to experimenters, the development of bench scale experimental variations of this type and larger than bench scale heat release experiments should be approached with caution until the potential hazards are more clearly defined.

13. A better understanding of the microstructure of the waste particles might assist in the development of an understanding of the mechanisms which control leaching. Therefore, a more advanced examination of these waste features through the use of techniques such as auger electron and transmission electron microscopy, is recommended.

14. The development of a characterization protocol for the determination of AFBC waste properties should continue. In addition to the definition of a laboratory protocol, a battery of simple, inexpensive screening tests for rapid field use should also be developed.

15. At least some AFBC residues have been indicated to possess properties which are unique in comparison to other coal combustion wastes. If further studies verify that

these properties are common and of significance for environmentally safe waste management, then the development of special handling and disposal methods for wastes of this nature will need to be initiated. In the interim, it is recommended that any waste management and disposal considerations for AFBC wastes, take the results of this study into consideration.

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APPENDIX

APPENDIX

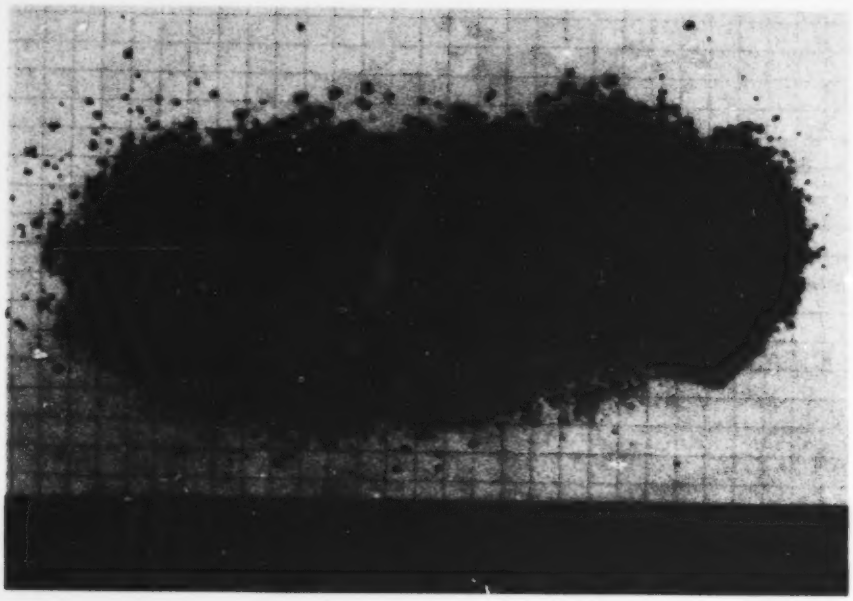

FIGURE A-1 MINTO BED MATERIAL

FIGURE A-2 DEVCO BED MATERIAL

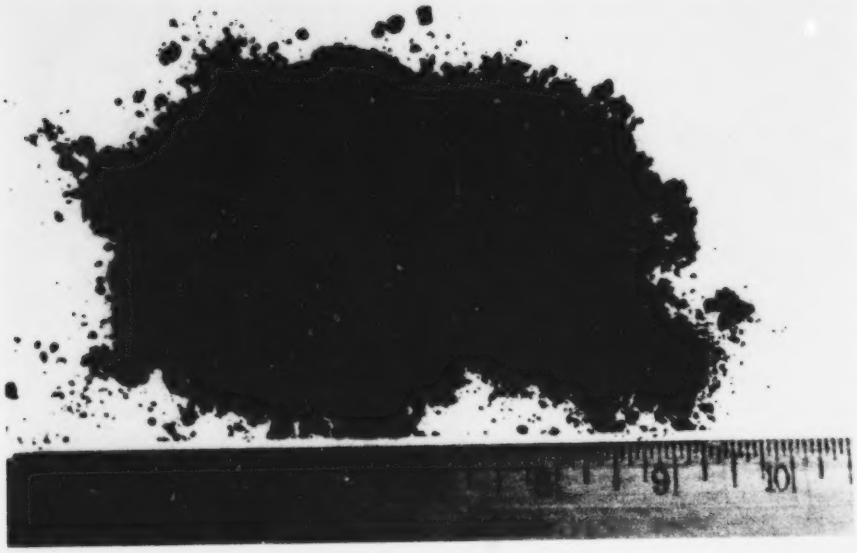

FIGURE A-3 DEVCO BAGHOUSE MATERIAL

FIGURE A-4 COLUMN

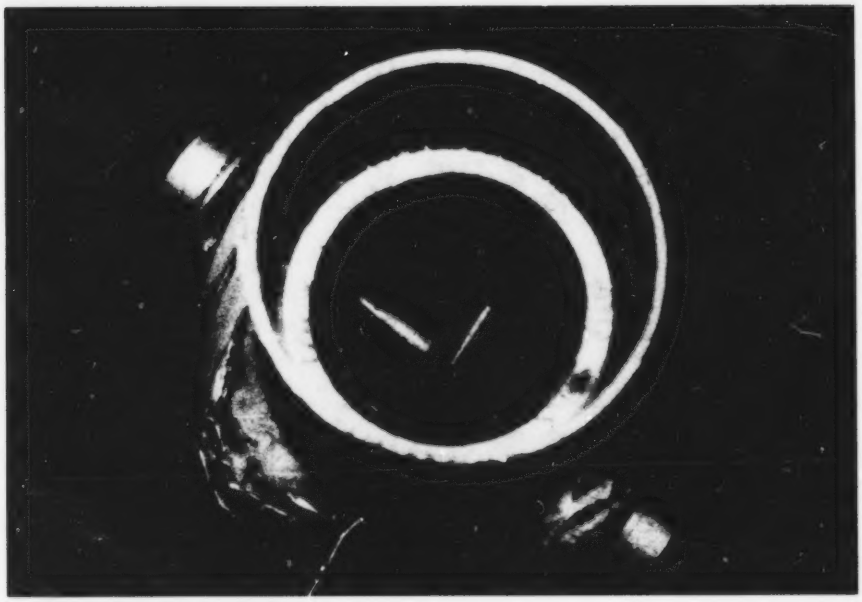

FIGURE A-5 TOP VIEW OF COLUMN (note thermometer probe)

TABLE A-1 pH, CONDUCTIVITY, TOTAL DISSOLVED SOLIDS AND WEIGHT LOSS OF DEVCO BED MATERIAL LEACHATES

Cycle	Leaching Condition *											
	Distilled Water Medium						Acidic Medium					
	4:1			20:1			4:1			20:1		
	pH	Cond	TDS	pH	Cond	TDS	pH	Cond	TDS	pH	Cond	TDS
1	11.95	8.5	2210	11.90	8.6	4310	12.0	13.1	13 400	12.0	13.4	13 400
2	11.45	8.1	4110	12.00	8.4	4120	12.0	12.9	13 500	12.1	13.0	13 200
3	11.95	8.0	3870	11.65	8.1	4180	11.8	12.4	12 900	11.95	12.7	12 900
4	11.85	7.6	3810	12.00	8.1	4250	12.05	12.5	12 100	10.45	8.0	11 700
5	11.90	7.9	3710	11.95	7.9	4150	11.95	12.2	12 200	7.60	7.6	11 900
6	11.95	7.8	3690	11.90	8.0	4060	11.95	12.3	12 400	6.15	7.6	11 800
7	11.85	7.8	3430	12.00	8.0	4020	11.95	12.1	12 700	4.7	6.7	8 970
8	11.75	7.9	3660	11.90	7.9	3940	11.90	12.2	12 900	4.3	5.4	7 230
9	11.80	7.8	3740	11.80	7.6	3310	11.80	12.2	12 800	4.2	5.0	6 580
10	11.75	8.4	3690	11.90	7.0	2350	11.85	11.95	12 600	4.2	3.2	4 040
Original Weight (g)		400.0			90.0			400.0			90.0	
Final Weight (g)		397.8			30.3			381.9			15.4	
Percent Loss		0.55			66.3			4.53			82.9	

* Note: Cond - (mS/cm)
TDS - (mg/L)

TABLE A-2 pH, CONDUCTIVITY, TOTAL DISSOLVED SOLIDS AND WEIGHT LOSS OF DEVCO BAGHOUSE MATERIAL LEACHATES

Cycle	Leaching Condition *											
	Distilled Water Medium						Acidic Medium					
	4:1			20:1			4:1			20:1		
	pH	Cond	TDS	pH	Cond	TDS	pH	Cond	TDS	pH	Cond	TDS
1	11.0	5.8	3680	11.05	4.5	3990	10.95	12.9	16 000	8.25	9.5	13 200
2	10.55	5.5	3410	10.85	3.8	2640	9.95	11.7	14 400	5.70	8.7	11 800
3	10.35	3.7	3330	10.70	1.7	1550	9.00	9.0	12 400	4.70	6.5	8 730
4	10.20	3.1	3080	10.80	.79	440	8.00	8.6	12 200	4.50	5.8	7 510
5	10.20	2.9	3030	10.75	.57	378	7.60	8.3	11 900	4.40	3.9	4 710
6	10.20	2.7	2880	10.70	.50	230	7.20	8.3	11 700	4.30	3.4	3 830
7	10.25	2.6	2880	10.70	.55	300	7.10	8.1	11 300	4.25	3.3	3 840
8	10.15	2.5	2800	10.65	.46	247	7.00	8.5	11 800	4.25	3.2	3 690
9	10.10	2.5	2910	10.60	.39	244	6.70	8.8	12 500	4.25	3.1	3 490
10	10.00	2.5	2730	10.50	.38	235	6.35	8.8	12 300	4.25	3.2	3 630
11	10.00	2.45	2920	10.40	.32	259	5.75	7.90	11 100	4.35	3.15	3 950
12	10.05	2.25	2430	10.45	.32	177	5.35	7.40	9 900	4.35	3.20	3 610
13	9.95	2.00	2050	10.20	.36	398	4.90	7.10	9 410	4.35	3.60	4 490
14	10.00	1.00	1490	10.25	.29	195	4.80	6.70	8 740	4.35	3.40	3 830
15	10.05	.99	872	10.20	.30	221	4.65	6.25	8 510	4.35	3.10	3 690
16	10.45	.71	568	10.15	.28	182	4.65	5.70	7 700	4.35	3.10	3 530
17	10.40	.63	454	10.25	.28	183	4.45	5.80	7 370	4.35	3.20	3 610
18	10.35	.55	439	9.90	.28	264	4.90	5.60	7 110	4.35	3.10	3 580
19	10.45	.49	322	10.10	.27	184	4.35	5.40	6 680	4.35	3.10	3 560
20	10.40	.45	342	10.20	.26	220	4.35	5.50	6 910	4.35	3.10	3 540
Original Weight (g)	472.5			94.5			472.5			94.5		
Final Weight (g)	427.1			76.3			403.1			64.4		
Percent Loss	9.61			19.3			14.7			31.9		

* Note: 4:1, 20:1 - liquid to solid ratio
Cond - (mS/cm)
TDS - (mg/L)

TABLE A-3 pH, CONDUCTIVITY, TOTAL DISSOLVED SOLIDS AND WEIGHT LOSS OF MINTO BED MATERIAL LEACHATES

Cycle	Leaching Condition *											
	Distilled Water Medium						Acidic Medium					
	4:1			20:1			4:1			20:1		
	pH	Cond	TDS	pH	Cond	TDS	pH	Cond	TDS	pH	Cond	TDS
1	12.05	9.6	4 430	12.10	8.8	4 650	12.05	13.0	13 600	12.10	13.3	13 900
2	12.05	9.7	4 490	12.10	9.6	4 200	12.05	14.4	13 400	12.05	14.0	13 300
3	11.95	9.1	4 190	11.95	9.0	4 180	11.95	14.1	13 300	11.95	13.1	12 900
4	11.90	9.4	4 370	11.95	9.0	4 180	11.95	13.8	13 300	11.40	8.6	11 600
5	11.95	9.3	4 380	11.95	9.0	4 160	11.95	13.6	13 600	6.55	8.1	12 000
6	11.85	9.3	4 350	11.90	8.9	3 770	11.85	13.7	13 300	4.65	6.8	9 160
7	11.85	9.1	4 200	11.90	8.3	2 810	11.85	13.5	13 011	4.35	5.5	6 800
8	11.90	9.0	4 210	11.90	7.6	2 040	11.90	13.5	12 800	4.30	3.6	4 110
9	11.90	9.2	4 310	12.00	7.3	1 750	12.00	13.4	13 100	4.30	3.2	3 720
10	11.85	9.1	4 180	11.90	6.6	1 510	11.90	13.5	13 000	4.25	3.2	3 670
11	11.90	8.60	3 810	11.75	2.85	844	11.95	13.40	12 700	4.35	3.10	3 650
12	11.90	8.80	3 610	11.50	1.35	377	11.95	13.20	12 300	4.35	3.10	3 510
13	11.80	8.80	3 570	11.20	.89	354	11.80	13.00	12 600	4.35	3.10	3 570
14	11.85	8.60	3 650	11.15	.72	342	11.85	13.00	12 100	4.35	3.10	3 560
15	11.85	8.60	3 630	11.00	.61	280	11.90	12.90	12 400	4.35	3.10	3 470
16	12.05	8.50	3 610	11.15	.54	221	12.05	12.70	12 600	4.35	3.10	3 490
17	11.95	8.80	3 730	11.00	.50	218	11.95	13.00	12 400	4.35	3.10	3 510
18	11.90	8.50	3 570	10.90	.39	228	11.95	12.90	12 700	4.35	3.10	3 580
19	11.90	8.50	3 500	10.80	.34	154	11.95	12.80	12 600	4.30	3.10	3 530
20	11.85	8.50	3 500	11.20	.95	454	11.95	12.60	12 700	4.35	3.10	3 510
Original Weight (g)	450.0			90.0			450.0			90.0		
Final Weight (g)	400.1			41.2			315.3			32.7		
Percent Loss	11.1			54.2			29.9			63.7		

* Note: 4:1, 20:1 - liquid to solid ratio
Cond - (mS/cm)
TDS - (mg/L)

TABLE A-4 CHARACTERIZATION OF LEACHING MEDIA AND MINTO BED MATERIAL LEACHATES (4:1)

Cycle	Medium	Medium	1		2		4		6		10		15		20	
Parameter/Medium	DI (distilled water)	Acidic	DI	Acidic	DI	Acidic	DI	Acidic	DI	Acidic	DI	Acidic	DI	Acidic	DI	Acidic
Aluminum	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01
Ammonia	0.04	0.04	0.05	0.07	-	-	0.03	0.01	-	-	0.07	0.05	0.04	0.04	0.03	0.03
Arsenic	< 0.005	< 0.005	< 0.005	< 0.005	-	-	< 0.005	< 0.005	-	-	< 0.005	< 0.005	-	-	-	-
Barium	< .005	< .005	.165	.211	.009	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005
Beryllium	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005
Boron	< .004	< .004	.045	.057	.044	.043	.032	.041	.044	.038	.034	.038	.038	.038	.035	.033
Cadium	< .01	< .01	.02	.04	.03	.04	.02	.03	.04	.03	.02	.03	.04	.04	.03	.04
Calcium	< .01	< .01	1550	2950	1580	2730	1600	2880	1570	2800	1510	2770	1330	2500	1340	2500
Chloride	< 2	24	7	6	-	-	< 2	< 2	-	-	< 2	< 2	-	-	-	-
Chromium	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01
Cobalt	< .05	< .05	< 05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05
Copper	.058	.017	< .008	.010	< .008	< .008	< .008	< .008	.010	.010	< .008	< .008	.010	.009	.010	< .008
Cyanide (free)	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01
Cyanide (complexed)	< .01	< .01	< .01	< .01	.	.	.	.	.	.	.	.	.	.	.	.
Fluoride	0.04	0.09	0.76	0.70	-	-	0.69	0.80	-	-	0.76	0.91	-	-	-	-
Iron	< .01	< .01	.08	.14	.12	.18	.08	.11	.15	.18	.10	.14	.15	.16	.12	.16
Lead	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05
Magnesium	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01
Manganese	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01
Molybdenum	< .3	< .3	< .3	< .3	< .3	< .3	< .3	< .3	< .3	< .3	< .3	< .3	< .3	< .3	< .3	< .3
Nickel	< .05	< .05	.11	.15	.14	.16	.11	.14	.14	.17	.12	.13	.16	.16	.14	.16
Phosphorus	< .6	< .6	1.0	1.6	1.3	1.6	.9	1.4	1.3	1.6	1.1	1.3	1.3	1.5	1.3	1.5
Potassium	< 1	< 1	12	13	2	2	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Silicon	< .05	< .05	< .05	< .05	.08	< .05	< .05	< .05	.13	.45	< .05	.12	.11	.11	.07	.07
Silver	< 0.005	< 0.005	< .005	.010	.008	.008	< .005	< .005	.013	.008	.009	< .005	.015	< .005	.011	< .005
Sodium	< 1	944	< 1	950	< 1	943	< 1	922	< 1	1000	< 1	926	< 1	1000	< 1	976
Strontium	.001	< .001	5.33	4.69	1.70	1.36	.787	.529	.487	.120	.442	.521	.906	< .001	.016	< .001
Sulphate	< .2	0.5	1590	1610	1420	1270	1410	1600	1240	1080	1340	1440	1180	1060	1210	1320
Thorium (µg/L)	< 3.5	< 3.5	< 3.5	< 3.5	-	-	< 3.5	< 3.5	-	-	< 3.5	< 3.5	< 3.5	< 3.5	< 3.5	< 3.5
Titanium	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005
Uranium (µg/L)	< 3.0	< 3.0	< 3.0	< 3.0	-	-	< 3.0	< 3.0	-	-	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0
Vanadium	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005
Zinc	.08	.06	.12	.14	.16	.19	.12	.14	.17	.18	.12	.17	.17	.18	.16	.19
Zirconium	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05
Acidity as $CaCO_3$	< 5	2840	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
COD	<10	-	20	-	-	-	< 10	-	-	-	< 10	-	< 10	-	< 10	-
Hardness as $CaCO_3$	0.44	1.43	4000	7700	4000	7700	4000	7200	3800	7300	4100	7200	3600	7000	35	7000

Note: all results are expressed in mg/L unless otherwise indicated

TABLE A-5 CHARACTERIZATION OF MINTO BED MATERIAL LEACHATES (20:1)

Cycle	1		2		4		6		10		15		20	
Parameter/Medium	DI (distilled water)	Acidic	DI	Acidic	DI	Acidic	DI	Acidic	DI	Acidic	DI	Acidic	DI	Acidic
Aluminum	< .01	< .01	< .01	< .01	< .01	< .01	< .01	37.0	< .01	7.35	2.90	3.06	1.79	1.44
Ammonia	0.03	0.05	-	-	0.06	0.04	-	-	0.07	0.10	0.02	0.02	0.04	0.04
Arsenic	< 0.005	< 0.005	-	-	< 0.005	< 0.005	-	-	< 0.005	< 0.005	-	-	-	-
Barium	< .005	< .005	< .005	< .005	< .005	< .005	< .005	.019	< .005	.163	< .005	< .005	< .005	< .005
Beryllium	< .005	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	.0056	< .0005	.0005	< .0005	< .0005	< .0005	< .0005
Boron	.042	.047	.033	.049	.033	.050	.027	.121	.019	< .004	.005	< .004	.011	< .004
Cadium	.02	.04	.03	.05	.03	.03	.03	.03	.01	< .01	< .01	< .01	< .01	< .01
Calcium	1630	2960	1570	2800	1590	2050	1370	1310	730	28.1	84.2	17.4	130	12.1
Chloride	< 2	< 2	< 2	< 2	< 2	< 2	< 2	23	< 2	98	< 2	104	< 2	85
Chromium	< .01	< .01	< .01	< .01	< .01	< .01	< .01	.02	< .01	< .01	< .01	< .01	< .01	< .01
Cobalt	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05
Copper	< .008	.010	< .008	.010	< .008	< .008	< .008	.150	< .008	.071	< .008	.051	< .008	.033
Cyanide (free)	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01
Cyanide (complexed)	< .01	< .01	-	-	-	-	-	-	-	-	-	-	-	-
Fluoride	0.65	0.73	0.65	0.89	0.73	1.05	0.72	0.95	0.04	< 0.01	0.42	< 0.01	0.39	< 0.01
Iron	.11	.14	.12	.18	.10	.10	.09	2.18	.07	2.89	.02	1.50	.02	.78
Lead	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05
Magnesium	< .01	< .01	< .01	< .01	< .01	.06	< .01	33.9	< .01	.75	.02	.25	.08	.14
Manganese	< .01	< .01	< .01	< .01	< .01	< .01	< .01	1.45	< .01	.23	< .01	.11	< .01	.07
Molybdenum	< .3	< .3	< .3	< .3	< .3	< .3	< .3	< .3	< .3	< .3	< .3	< .3	< .3	< .3
Nickel	.11	.16	.12	.17	.12	.13	.12	.16	.07	< .05	< .05	< .05	< .05	< .05
Phosphorus	1.1	1.5	1.2	1.6	1.0	1.1	1.2	1.3	.7	< .6	< .6	< .6	< .6	< .6
Potassium	2	< 1	< 1	< 1	< 1	< 1	< 1	3	< 1	< 1	< 1	< 1	< 1	< 1
Silicon	.08	< .05	< .05	.08	.05	5.81	.11	74.3	.21	11.6	3.62	6.21	4.22	3.47
Silver	.010	.010	< .005	.009	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005
Sodium	< 1	927	< 1	957	< 1	924	< 1	957	< 1	904	< 1	952	< 1	939
Strontium	1.33	1.07	.412	.113	.284	.226	.257	.920	< .001	.014	.071	.006	.026	.002
Sulphate	1590	1550	1250	1270	1380	1590	1300	1490	25	25	79	10	.45	10
Thorium (µg/L)	< 3.5	< 3.5	-	-	< 3.5	< 3.5	-	-	< 3.5	< 3.5	< 3.5	< 3.5	< 3.5	< 3.5
Titanium (µg/L)	< .005	< .005	< .005	< .005	< .005	< .005	< .005	.007	< .005	< .005	< .005	< .005	< .005	< .005
Uranium	< 3.0	< 3.0	-	-	< 3.0	< 3.0	-	-	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0
Vanadium	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005
Zinc	.12	.16	.16	.19	.12	.15	.14	.44	.11	.14	.09	.09	.09	.06
Zirconium	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05
Acidity as $CaCO_3$	< 5	< 5	< 5	< 5	< 5	< 5	< 5	1950	< 5	3500	< 5	3530	< 5	3600
COD	< 10	-	-	-	< 10	-	-	-	< 10	-	< 10	-	< 10	-
Hardness as $CaCO_3$	7700	8000	4100	7700	3900	5300	3800	3650	1800	90	215	52	360	42

Note: all results are expressed in mg/L unless otherwise indicated

TABLE A-6 CHARACTERIZATION OF DEVCO BAGHOUSE MATERIAL LEACHATES (4:1)

Cycle	1		2		4		6		10		15		20	
Parameter/Medium	DI (distilled water)	Acidic	DI	Acidic	DI	Acidic	DI	Acidic	DI	Acidic	DI	Acidic	DI	Acidic
Aluminum	< .01	< .01	.14	< .01	< .01	< .01	.47	.54	< .01	< .01	.54	61.1	1.93	71.9
Ammonia	2.5	1.9	-	-	0.07	0.09	-	-	0.26	0.15	0.16	0.09	0.07	0.09
Arsenic	0.005	< 0.024	0.005	< 0.005	< 0.005	< 0.103	0.006	0.039	0.036	0.044	0.017	0.091	< 0.005	< 0.005
Barium	1.14	1.12	.482	.578	.171	.044	.146	< .005	.101	.102	.095	< .005	.127	< .005
Beryllium	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005	.0322	< .0005	.0497
Boron	.110	.200	.068	.208	.045	.727	.055	3.65	.048	1.70	.041	.290	.038	.106
Cadium	.04	.05	.03	.05	.02	.03	.02	.03	.02	.03	.02	.03	.01	.02
Calcium	2580	3910	1240	2850	838	2110	796	2050	729	2130	210	1110	72.7	843
Chloride	3900	3900	1280	1560	236	198	49	66	4	88	9	10	6	61
Chromium	.23	.16	.19	.18	.13	.07	.07	.02	.02	< .01	.02	.09	< .01	.10
Cobalt	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	.06	< .05
Copper	.015	.024	< .008	.010	< .008	< .008	< .008	< .008	< .008	.021	< .008	.151	< .008	.225
Cyanide (free)	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01
Cyanide (complexed)	< .01	< .01	-	-	-	-	-	-	-	-	-	-	-	-
Fluoride	0.80	0.90	-	-	0.87	0.91	-	-	1.14	1.06	-	-	-	-
Iron	.13	.17	.11	.17	.08	.20	.11	.18	.07	.16	.07	7.66	.05	11.0
Lead	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05
Magnesium	.32	.94	.44	1.80	1.02	10.4	1.11	11.5	1.18	21.2	.39	10.6	.11	2.48
Manganese	< .01	< .01	< .01	< .01	< .01	< .01	< .01	.06	< .01	4.69	< .01	1.64	< .01	.42
Molybdenum	1.5	1.7	.8	1.0	.4	.6	< .3	< .3	< .3	< .3	< .3	< .3	< .3	< .3
Nickel	.4	.18	.12	.18	.07	.13	.10	.13	.08	.25	.06	.29	< .05	.16
Phosphorus	1.4	1.8	1.1	1.8	.8	1.3	1.1	1.3	.8	1.3	.6	1.0	< .6	1.0
Potassium	126	146	53	60	27	16	14	6	5	3	4	5	3	2
Silicon	6.40	8.09	10.7	9.34	12.1	2.62	11.1	.89	8.85	20.6	8.01	95.0	6.81	72.9
Silver	.005	.005	.006	.008	< .005	< .005	.010	< .005	< .005	< .005	.006	< .005	.008	< .005
Sodium	44	970	22	926	11	901	7	877	2	942	2	978	2	973
Strontium	24.4	25.0	9.64	11.1	5.86	4.08	3.45	2.08	2.06	2.40	.727	3.06	.335	.988
Sulphate	1180	1120	-	-	1440	1470	-	-	1440	1390	-	-	-	-
Thorium (µg/L)	< 3.5	< 3.5	-	-	< 3.5	< 3.5	-	-	< 3.5	< 3.5	< 3.5	< 3.5	< 3.5	< 3.5
Titanium	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	.120	< .005	.073
Uranium (µg/L)	< 3.0	< 3.0	-	-	< 3.0	< 3.0	-	-	< 3.0	21	< 3.0	18	< 3.0	11
Vanadium	< .005	< .005	.020	.041	.055	.072	.082	< .005	.071	.042	.079	.024	.072	< .005
Zinc	.14	.16	.13	.19	.11	.13	.13	.18	.11	.16	.11	.74	.08	.37
Zirconium	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05
Acidity as $CaCO_3$	< 5	50	< 5	< 5	< 5	6	< 5	18	< 5	122	< 5	2540	< 5	3400
COD	46	-	-	-	< 10	-	-	-	< 10	-	< 10	-	< 10	-
Hardness as $CaCO_3$	6500	10 300	-	-	2000	5450	-	-	1900	5800	800	3150	190	2410

Note: all results are expressed in mg/L unless otherwise indicated

TABLE A-7 CHARACTERIZATION OF DEVCO BAGHOUSE MATERIAL LEACHATES (20:1)

Cycle	1		2		4		6		10		15		20	
Parameter/Medium	DI (distilled water)	Acidic	DI	Acidic	DI	Acidic	DI	Acidic	DI	Acidic	DI	Acidic	DI	Acidic
Aluminum	< .01	< .01	.42	2.88	1.02	91.7	3.46	40.5	6.18	22.1	5.71	24.2	5.60	11.9
Ammonia	0.65	0.03	-	-	0.13	0.25	-	-	0.10	0.18	0.04	0.07	0.04	0.05
Arsenic	< 0.005	0.053	< 0.005	< 0.005	< 0.005	0.238	< 0.005	0.104	0.022	0.081	0.029	0.089	0.032	0.042
Barium	.434	0.005	.289	< .005	.128	< .005	.103	.433	.051	1.44	.028	.346	.019	.084
Beryllium	< .0005	< .0005	< .0005	< .0005	< .0005	.0494	< .0005	.0217	< .0005	.0063	< .0005	.0104	< .0005	.0020
Boron	.090	2.17	.082	1.69	.043	.234	.049	.051	.060	.016	.060	.022	.063	< .004
Cadmium	.03	.04	.03	.05	< .01	.02	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01
Calcium	1150	2570	716	2010	124	976	75.5	56.0	55.9	20.1	51.4	17.3	43.6	5.50
Chloride	890	836	-	-	< 2	10	-	-	< 2	55	-	-	-	-
Chromium	.09	< .01	.05	< .01	< .01	.08	< .01	.04	< .01	.02	.01	.02	< .01	< .01
Cobalt	.05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05
Copper	< .008	.012	< .008	.027	< .008	.195	< .008	.124	< .008	.093	< .008	.085	< .008	.063
Cyanide (free)	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01	< .01
Cyanide (complexed)	< .01	< .01	-	-	-	-	-	-	-	-	-	-	-	-
Fluoride	0.91	1.37	0.73	1.20	0.40	1.06	0.14	0.19	0.08	0.09	0.01	0.03	0.03	0.05
Iron	.08	.14	.08	.74	.02	16.9	.02	11.2	< .01	7.31	.05	7.05	.02	4.14
Lead	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05
Magnesium	.18	17.3	.25	15.3	.12	5.70	.06	1.03	.06	.62	.08	.63	.05	.26
Manganese	< .01	.12	< .01	3.35	< .01	.70	< .01	.13	< .01	.24	< .01	.08	< .01	.04
Molybdenum	.5	.8	< .3	< .3	< .3	< .3	< .3	< .3	< .3	< .3	< 3	< .3	< .3	< .3
Nickel	.09	.14	.08	.37	< .05	.17	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05
Phosphorus	1.0	1.5	1.0	1.6	< .6	1.1	< .6	.6	< .6	< .6	< .6	< .6	< .6	< .6
Potassium	27	29	7	9	< 1	1	1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Silicon	5.35	1.53	11.2	43.5	7.56	104	4.87	46.1	3.00	30.8	3.02	34.6	2.30	19.7
Silver	< .005	< .005	.007	.012	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005	< .005
Sodium	10	940	2	984	3	944	1	979	< 1	941	2	990	< 1	937
Strontium	5.91	5.39	2.26	2.89	.716	1.92	.320	.716	.171	.263	.096	.253	.059	.144
Sulphate	1550	1640	1490	1220	250	1400	470	72	75	77	67	10	63	8
Thorium (µg/L)	< 3.5	< 6.8	-	-	< 3.5	5.8	-	-	< 3.5	< 3.5	< 3.5	< 3.5	< 3.5	< 3.5
Titanium	< .005	< .005	< .005	< .005	< .005	.246	< .005	.084	< .005	.079	< .005	.079	< .005	.068
Uranium (µg/L)	< 3.0	17	-	-	< 3.0	17	-	-	< 3.0	4.7	< 3.0	3.7	< 3.0	< 3.0
Vanadium	< .005	< .005	.046	< .005	.033	.034	.049	.014	.037	< .005	.043	.014	.021	.005
Zinc	.11	.14	.13	.25	.07	.50	.10	.22	.07	.12	.08	.13	.10	.10
Zirconium	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05
Acidity as $CaCO_3$	< 5	< 5	< 5	214	< 5	2800	< 5	3500	< 5	3550	< 5	3600	< 5	3600
COD	< 10	-	-	-	20	-	-	-	< 10	-	< 10	-	< 10	-
Hardness as $CaCO_3$	2800	6180	-	-	380	2630	-	-	1/2	65	120	51	110	2000

NOTE: all results expressed in mg/L unless otherwise indicated

TABLE A-8 CHARACTERIZATION OF DEVCO BED MATERIAL LEACHATES (4:1)

Cycle	1		4		10	
Parameter/Medium	DI (distilled water)	Acidic	DI	Acidic	DI	Acidic
Aluminum	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Ammonia	0.15	0.11	0.05	0.05	0.05	0.09
Arsenic	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Barium	.073	0.77	.032	< .005	< .005	< .005
Beryllium	.0005	< .0005	< .0005	< .0005	< .0005	< .0005
Boron	.078	.082	.044	.053	.031	.040
Cadmium	.03	.04	.02	.04	.02	.03
Calcium	1530	2780	1330	2680	1320	2600
Chloride	7	9	< 2	< 2	< 2	< 2
Chromium	< .01	< .01	< .01	< .01	< .01	< .01
Cobalt	< .05	< .05	< .05	< .05	< .05	< .05
Copper	.010	.010	< .008	.013	.009	.010
Cyanide free	< .01	< .01	< .01	< .01	< .01	< .01
Cyanide complexed	< .01	< .01	-	-	-	-
Fluoride	0.70	0.65	0.64	0.61	0.61	0.75
Iron	.12	.14	.10	.14	.08	.15
Lead	< .05	< .05	< .05	< .05	< .05	< .05
Magnesium	< .01	< .01	< .01	< .01	< .01	< .01
Manganese	.01	< .01	< .01	< .01	< .01	< .01
Molybdenum	< .3	< .3	< .3	< .3	< .3	< .3
Nickel	.13	.15	.11	.16	.12	.13
Phosphorus	1.1	1.4	1.0	1.4	1.0	1.3
Potassium	2	3	< 1	< 1	< 1	< 1
Silicon	< .05	< .05	< .05	< .05	< .05	< .05
Silver	.011	.008	< .005	.011	.007	< .005
Sodium	2	967	< 1	939	< 1	917
Strontium	2.99	2.96	2.88	2.01	.836	.705
Sulphate	1550	1480	1360	1320	1220	1150
Thorium (µg/L)	< 3.5	< 3.5	5.6	< 3.5	4.8	< 3.5
Titanium	< .005	< .005	< .005	< .005	< .005	< .005
Uranium (µg/L)	< 3.0	< 3.0	< 3.0	6.0	< 3.0	< 3.0
Vanadium	< .005	< .005	< .005	< .005	< .005	< .005
Zinc	.13	.13	.12	.14	.12	.18
Zirconium	< .05	< .05	< .05	< .05	< .05	< .05
Acidity as $CaCO_3$	< 5	< .5	< 5	< 5	< 5	< 5
COD	54	-	16	-	< 10	-
Hardness as $CaCO_3$	3800	7500	3500	7000	3500	6800

Note: all results are expressed in mg/L unles otherwise indicated

TABLE A-9 CHARACTERIZATION OF DEVCO BED MATERIAL LEACHATES (20:1)

Cycle	1		4		10	
Parameter/Medium	DI (distilled water)	Acidic	DI	Acidic	DI	Acidic
Aluminum	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	10.6
Ammonia	0.15	0.07	0.04	0.07	0.03	0.07
Arsenic	< 0.005	< 0.005	< 0.005	0.027	< 0.005	< 0.005
Barium	< .005	< .005	< .005	< .005	< .005	.023
Beryllium	< .0005	< .0005	< .0005	< .0005	< .0005	< .0005
Boron	.111	.058	.038	.314	.025	.015
Cadmium	.02	.04	.03	.03	.02	< .01
Calcium	1480	2870	1490	1910	963	112
Chloride	< 2	< 2	< 2	9	< 2	141
Chromium	< .01	< .01	< .01	< .01	< .01	0.2
Cobalt	< .05	< .05	< .05	< .05	< .05	< .05
Copper	.008	.009	.010	< .008	< .008	.064
Cyanide free	< .01	< .01	< .01	< .01	< .01	< .01
Cyanide complexed	< .01	< .01	-	-	-	-
Fluoride	0.73	0.68	0.65	1.33	0.26	0.15
Iron	.10	.14	.11	.08	.07	12.6
Lead	< .05	< .05	< .05	< .05	< .05	< .05
Magnesium	.09	< .01	< .01	10.2	< .01	1.19
Manganese	< .01	< .01	< .01	< .01	< .01	.43
Molybdenum	< .3	< .3	< .3	< .3	< .3	< .3
Nickel	.11	.16	.12	.12	.08	< .05
Phosphorus	1.1	1.5	1.1	1.1	.9	< .6
Potassium	< 1	< 1	< 1	< 1	< 1	< 1
Silicon	.11	< .05	< .05	10.1	.08	16.5
Silver	.009	.011	.011	< .005	< .005	< .005
Sodium	6	926	< 1	890	< 1	908
Strontium	.986	.713	.264	.237	< .001	.037
Sulphate	1590	1480	1620	1600	400	200
Thorium (µg/L)	4.3	< 3.5	< 3.5	< 3.5	< 3.5	< 3.5
Titanium	< .005	< .005	< .005	< .005	< .005	0.11
Uranium (µg/L)	2.7	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0
Vanadium	< .005	< .005	< .005	.032	< .005	< .005
Zinc	.14	.14	.13	.13	.12	.12
Zirconium	< .05	< .05	< .05	< .05	< .05	< .05
Acidity as $CaCO_3$	< 5	< .5	< 5	< 5	< 5	3400
COD	16	-	< 10	-	< 10	-
Hardness as $CaCO_3$	3900	7500	3800	5250	2500	320

Note: all results are expressed in mg/L unless otherwise indicated

TABLE A-10 DEVCO BED SOLIDS AFTER LEACHING (20 CYCLES)

Parameters	Conditions			
	Acidic		Distilled Water	
	4:1	20:1	4:1	20:1
Aluminum	15 300	128 000	15 500	67 200
Barium	44.8	426	41.8	219
Boron	52.9	152	56.6	121
Beryllium	< .05	2.84	< .05	1.01
Calcium	308 000	20 900	337 000	244 000
Cadmium	5	2	5	5
Cobalt	< 5	17	< 5	6
Chromium	12	73	12	46
Copper	8.7	53.7	10.7	46.7
Iron	12 700	57 400	10 700	35 100
Lead	< 5	140	15	60
Potassium	1 900	15 600	2 500	8 700
Magnesium	2 430	4 110	2 650	8 700
Manganese	428	1 560	368	1 130
Molybdenum	< 1	< 1	< 1	< 1
Sodium	200	12 800	1 800	1 800
Nickel	26	36	30	35
Phosphorus	290	1 050	310	700
Silicon (%)	3.39	17.0	2.94	8.81
Silver	3.6	1.5	4.4	3.8
Strontium	19.5	445	17.6	242
Titanium	896	4 070	993	2 050
Vanadium	16.7	106	15.9	60.6
Zinc	29	85	31	82
Zirconium	24	90	26	57

Note: all units are expressed in µg/g unless otherwise indicated

TABLE A-11 MINTO BED SOLIDS AFTER LEACHING (20 CYCLES)

Parameters	Conditions			
	Acidic		Distilled Water	
	4:1	20:1	4:1	20:1
Aluminum	57 100	187 000	40 000	81 800
Barium	198	272	126	265
Boron	292	400	197	353
Beryllium	1.19	4.40	.56	3.12
Calcium	166 000	7 210	227 000	93 200
Cadmium	4	< 1	4	3
Cobalt	< 5	40	< 5	11
Chromium	12	23	11	31
Copper	22.7	15.5	18.4	101
Iron	15 100	23 500	13 300	31 800
Lead	< 5	< 5	< 5	< 5
Potassium	6 600	16 000	6 100	9 900
Magnesium	5 180	2 160	3 260	11 900
Manganese	547	391	386	1 040
Molybdenum	< 1	< 1	< 1	< 1
Sodium	1 400	6 100	600	1 500
Nickel	21	16	27	37
Phosphorus	1 970	1 600	760	1 360
Silicon (%)	7.98	19.8	5.96	16.3
Silver	2.3	1.3	3.1	2.6
Strontium	122	176	47.4	111
Titanium	548	991	574	1 200
Vanadium	18.5	34.4	15.9	39.6
Zinc	51	61	43	92
Zirconium	54	111	44	75

Note: all units are expressed as µg/g unless otherwise indicated

TABLE A-12 DEVCO BAGHOUSE SOLIDS AFTER LEACHING (20 CYCLES)

Parameters	Conditions			
	Acidic		Distilled Water	
	4:1	20:1	4:1	20:1
Aluminum	74 800	109 000	82 400	86 800
Barium	571	388	433	382
Boron	< 4	< 4	82.6	60.7
Beryllium	9.38	9.79	10.2	11.3
Calcium	20 300	20 600	108 000	96 800
Cadmium	5	2	7	7
Cobalt	20	20	20	27
Chromium	163	195	158	174
Copper	116	167	126	157
Iron	118 000	206 000	111 000	124 000
Lead	235	350	210	275
Potassium	10 100	16 800	10 600	11 800
Magnesium	2 450	4 260	4 330	5 040
Manganese	274	433	390	451
Molybdenum	< 1	< 1	< 1	< 1
Sodium	3 400	5 300	3 600	3 600
Nickel	119	168	130	144
Phosphorus	1 240	1 780	1 330	1 460
Silicon (%)	12.6	12.1	5.76	8.26
Silver	2.0	1.3	2.6	3.0
Strontium	537	795	592	672
Titanium	4 410	6 960	4 610	5 160
Vanadium	215	318	210	220
Zinc	164	241	170	202
Zirconium	80	124	90	98

Note: all units are expressed as µg/g unless otherwise indicated

TABLE A-13 X-RAY DIFFRACTION ANALYSES OF AFBC SOLID RESIDUES REMAINING AFTER LEACHING

Material	Compound	Original Sample	Leaching Conditions			
			4:1 Distilled Water	20:1 Distilled Water	4:1 Acid	20:1 Acid
Devco Baghouse	$CaSO_4$	40	-	-	-	-
	$CaSO_4 \cdot 2H_2O$	10	-	-	-	-
	γ- $CaSO_4$	-	-	-	-	-
	CaO	9	-	-	-	-
	$CaCO_3$	-	-	-	-	-
	SiO_2	13	-	10	18	13
Minto Bed	$CaSO_4$	73	-		-	
	$CaSO_4 \cdot 2H_2O$	-	38	insufficient	43	insufficient
	γ- $CaSO_4$	-	-	sample for	-	sample for
	CaO	90	-	analysis	-	analysis
	$CaCO_3$	-	-		-	
	SiO_2	9	14		15	
Devco Bed	$CaSO_4$	102	-		-	
	$CaSO_4 \cdot 2H_2O$	-	146	insufficient	120	insufficient
	γ- $CaSO_4$	-	-	sample for	-	sample for
	CaO	60	10	analysis	-	analysis
	$CaCO_3$	-	-		-	
	SiO_2	12	-		-	

Note: results reported in XRD peak height arbitrary units to illustrate trends only

(-) signifies not detected

TABLE A-14 THIRTY MINUTE AND TOTAL ALKALINITY OF AFBC COMBUSTION RESIDUES

a) Thirty-Minute Alkalinity of AFBC Residues

Sample	Equivalent-grams per kg sample	Neutralization Coefficient (ASTM C400-64)
Minto Bed	4.56	6.65×10^4
Devco Bd	6.65	4.56×10^4
Devco Baghouse	2.7	1.1×10^5

(b) Total Alkalinity of AFBC Residues

Sample	Equivalent-grams per kg sample	Total Neutralization Coefficient
Minto Bed	8.95	3.38×10^4
Devco Bed	9.0	3.36×10^4
Devco Baghouse	2.7	1.1×10^5

TABLE A-15 ELEMENTAL COMPOSITION OF SIEVE SIZES OF TWO AFBC COMBUSTION RESIDUES

Element	Minto Bed Material				Devco Bed Material			
	Sieve 10	Sieve 20	Sieve 40	< Sieve 40	Sieve 10	Sieve 20	Sieve 40	< Sieve 40
Ag	< .5	< .5	3.1	4.2	< .5	2.8	4.5	2.8
Al	86 100	10 700	21 200	5 690	92 400	47 200	8 060	3 600
Be	.33	1.11	< .05	< .05	1.63	< .05	< .05	< .(
Ca	24 600	231 000	386 000	376 000	123 000	343 000	381 000	418 000
Cd	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Co	5	5	5	11	30	5	12	5
Cr	10	10	2	7	58	18	13	5
Cu	49.5	15.6	20.2	32.6	34.6	12.9	9.4	8.(
Fe	17 300	10 800	12 000	17 300	20 000	12 300	12 800	11 900
K	100	9 500	2 100	1 000	17 100	4 800	1 200	300
Mg	3 540	2 660	3 930	3 540	4 020	2 540	2 140	2 240
Mn	562	327	485	562	268	472	491	515
Mo	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Na	300	2 000	500	300	4 000	900	300	400
Ni	42	35	43	42	44	43	45	40
P	766	970	750	760	1 000	560	370	310
Pb	< 5	< 5	< 5	< 5	155	30	< 5	< 5
Si	159	172	117	159	438	197	111	90.7
Th	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Ti	414	432	390	414	3 850	783	428	282
V	15.4	13.5	10.8	15.4	79.9	23.4	16.8	9.6
Zn	78	79	62	78	94	65	49	44
Zr	16	52	21	16	42	31	15	13

Note: analyses reported in µg/g

TABLE A-16 LEACHATES FROM STEEL COLUMN EXOTHERMIC TESTS OF AFBC COMBUSTION RESIDUES

Sample	pH (units)	Conductivity (mS/cm)	Total Solids (mg/L)	Total Dissolved (mg/L)
Minto Bed D.I.	12.4	8 000	5 280	5 130
Devco Bed D.I.	12.3	7 900	5 270	5 070
Devco Bed Acidic	12.3	12 000	17 400	17 000
Minto Bed Acidic	12.3	12 400	21 300	15 800
Acidic Medium	4.5	3 600	3 850	3 730
D.I. Medium	5.5	5	< 2	< 2